

DEVELOPMENT AND PERFORMANCE
EVALUATION OF
ZINC OXIDE/GRAPHENE/NICKEL FOAM
PHOTOANODE FOR PHOTOELECTROCHEMICAL
HYDROGEN PRODUCTION

NUR RABIATUL ADAWIYAH BINTI MOHD SHAH

UNIVERSITI KEBANGSAAN MALAYSIA

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PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

NUR RABIATUL ADAWIYAH BINTI MOHD SHAH

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NUR RABIATUL ADAWIYAH BINTI MOHD SHAH

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Nama penuh pengarang (Author's Full Name)	NUR RABIATUL ADAWIYAH BINTI MOHD SHAH		
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Nama Pelajar (Student name): NUR RABIATUL ADAWINAH No. Pendaftaran Pelajar (Student's Registration No.): BINTI MOHD SHAH P104897 Tarikh: 12 JUN 2026 (Date)		Nama Penyelia / Pengerusi JK Siswazah : PROF. MADYA DR. ROZAN (Supervisor's / Chairperson Supervision Committee Name) MOHAMAD YUNUS Tarikh: 12 / 06 / 2026 (Date)	

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged.

13 July 2026

NUR RABIATUL ADAWIYAH
BINTI MOHD SHAH
P104897

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ABSTRAK

Kecekapan pembelahan molekul air secara fotoelektrokimia (PEC) bergantung pada fotoelektrod, yang merupakan komponen utama dalam penukaran terus tenaga suria kepada tenaga kimia dalam bentuk hidrogen (H_2). Penggunaan bahan semikonduktor sebagai fotoelektrod sering menghadapi isu penggabungan semula cas dan kestabilan yang lemah dalam elektrolit. Sementara itu, zink oksida (ZnO) menawarkan mobiliti elektron yang tinggi dan mesra alam, sela jalurnya yang lebar (3.37 eV) menghadkan penyerapan cahaya ultralembayung dan menyebabkan penggabungan semula elektron-lohong yang pantas. Pengintegrasian grafin berpotensi meningkatkan prestasi secara signifikan, namun kecenderungannya untuk mengalami penggumpalan akibat sifat intrinsik dua-dimensinya masih merupakan cabaran utama dalam proses integrasi tersebut. Walaupun busa Nikel berpotensi untuk menjadi penyokong kepada grafin, mekanisme pemindahan cas antara ZnO , grafin, dan busa Nikel masih kurang difahami. Kajian ini bertujuan untuk menyiasat secara sistematik potensi fotoelektrod komposit ZnO /grafin/bus Nikel dalam meningkatkan prestasi PEC, serta menjelaskan mekanisme pemindahan cas melalui kaedah eksperimen dan teori fungsi ketumpatan (DFT). Pada peringkat awal, grafin disintesis pada busa Nikel melalui kaedah pemendapan wap kimia (CVD), dengan mengubah suai masa penyepuhlindapan (0 – 60 minit), kadar aliran metana (0 – 30 sccm), dan masa pertumbuhan (0 – 30 minit) bagi mendapatkan grafin yang berkualiti. Kemudian, grafin/bus Nikel yang terbaik digunakan sebagai substrat bagi pertumbuhan ZnO menggunakan kaedah hidroterma dengan variasi suhu tindak balas (150 – 220 °C) selama 8 jam. Struktur morfologi dan prestasi PEC ZnO /grafin/bus Nikel telah dicirikan, manakala pengiraan DFT dijalankan untuk memberikan pemahaman mengenai mekanisme pemindahan cas. Parameter CVD yang terbaik berjaya menghasilkan grafin yang berkualiti tinggi di atas busa Nikel pada masa penyepuhlindapan: 50 minit, kadar aliran metana: 10 sccm, dan masa pertumbuhan: 20 minit. Seterusnya, sintesis hidroterma pada suhu 200 °C berjaya menghasilkan nanorod ZnO yang mempunyai tahap kehabluran tinggi dengan nisbah panjang-kepada-diameter yang optimum serta liputan permukaan yang tinggi pada grafin/bus Nikel. Komposit ZnO /grafin/bus Nikel yang terbaik mencapai ketumpatan fotoarus yang tertinggi iaitu 29.04 mA/cm² pada 1.23 V melawan RHE dengan kadar penghasilan H_2 sebanyak 1.72 mL/jam. Prestasi unggul ini dikaitkan dengan kesan sinergistik antara komponen, di mana struktur berliang busa Nikel meningkatkan kebolehcapaian elektrolit serta menambah luas permukaan untuk tindak balas fotokatalitik, manakala pengintegrasian grafin berjaya menurunkan potensi onset fotoarus daripada 0.40 V kepada 0.20 V serta menggalakkan pemisahan dan pemindahan cas yang lebih cekap. Tambahan pula, kehadiran Na_2SO_3 sebagai agen penghapus lohong membantu mengurangkan kadar penggabungan semula elektron-lohong dengan bertindak balas secara pantas terhadap lohong yang terjana oleh cahaya, sekali gus meningkatkan lagi prestasi PEC. Analisis DFT menunjukkan bahawa konfigurasi *Zn-terminated ZnO/Top-fcc* grafin/Nikel merupakan struktur yang paling stabil dari segi tenaga ikatan antara muka, dan menyediakan laluan pemindahan elektron yang cekap, selari dengan keputusan eksperimen. Dapatan ini memberikan pemahaman asas yang jelas mengenai mekanisme pemindahan cas yang menunjukkan potensi besar komposit ZnO /grafin/bus Nikel dalam penghasilan H_2 suria yang cekap dan mampan.

ABSTRACT

Efficient photoelectrochemical (PEC) water splitting lies in the photoelectrode, a crucial component for directly converting solar energy into chemical energy in the form of hydrogen (H_2). The application of semiconductor materials as photoelectrodes is often suffer by rapid charge recombination and poor stability in electrolytes. Meanwhile, zinc oxide (ZnO) offers high electron mobility and environmental friendliness, its wide band gap (3.37 eV) limits ultraviolet light absorption and causes rapid electron-hole recombination. Integrating graphene can significantly enhance the performance, but its tendency toward aggregation due to its intrinsic two-dimensional nature remains a critical challenge in the fabrication process. Although nickel foam (Ni-foam) can support graphene, the charge transfer mechanism among ZnO, graphene, and Ni-foam remains poorly understood. This work aimed to systematically investigate the potential of ZnO/graphene/Ni-foam composite photoelectrode for enhanced PEC performance, as well to elucidate the underlying charge transfer mechanism using experimental and density functional theory (DFT) approaches. Graphene was first synthesized on Ni-foam via chemical vapor deposition (CVD), tailoring annealing time (0 – 60 minutes), methane flow rate (0 – 30 sccm), and growth time (0 – 30 minutes) for high quality graphene. The best graphene/Ni-foam were then used to hydrothermally grow ZnO on graphene/Ni-foam substrate, varying reaction temperatures (150 – 220 °C) for 8 hours. The morphological structure and PEC performance of ZnO/graphene/Ni-foam was characterized, and DFT calculations provided insights into charge transfer. The best CVD parameters produced high-quality graphene on Ni-foam at annealing time: 50 minutes, methane flow rate: 10 sccm, and growth time: 20 minutes. Hydrothermal synthesis at 200 °C formed highly crystalline ZnO nanorods with an optimized length-to-diameter ratio and high surface coverage across the graphene/Ni-foam. The best ZnO/graphene/Ni-foam composite achieved an outstanding photocurrent density of 29.04 mA/cm² at 1.23 V vs. RHE with a H_2 production rate of 1.72 mL/hour. This superior performance is attributed to the synergistic effects of each component within the composite system. The porous structure of the Ni-foam improves electrolyte accessibility and provides higher surface area for photocatalytic reactions, while the integration of graphene successfully lowers the photocurrent onset potential from 0.40 V to 0.20 V and facilitates more efficient charge separation and transfer. Furthermore, the presence of Na_2SO_3 as a hole scavenger suppresses electron-hole recombination by rapidly consuming photogenerated holes, thereby further enhancing the PEC performance. DFT studies revealed that the Zn-terminated ZnO/Top-fcc graphene/Ni configuration is the most stable regarding interfacial binding energy, and facilitating efficient electron transfer pathways, align with experimental result. These findings clearly provide the fundamental understanding of charge transfer mechanisms that highlight the high potential of ZnO/graphene/Ni-foam composites for efficient and sustainable solar H_2 production.

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LIST OF ABBREVIATIONS

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
APBE	Applied bias Photon-to-current Efficiency
CA	Chronoamperometry
CB	Conduction band
CCUS	Carbon, Capture, Utilization and Storage
CDD	Charge Density Different
CE	Counter electrode
CNT	Carbon Nanotube
CPE	Constant Phase Element
CVD	Chemical Vapor Deposition
DFT	Density Functional Theory
EDX	Elemental Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
FE	Faraday Efficiency
FESEM	Field Emission Scanning Electron Microscope
FTO	Fluorine-doped Tin Oxide
GC	Gas Chromatography
GGA	Generalized Gradient Approximation
GHG	Greenhouse Gases
GO	Graphene Oxide
HER	Hydrogen Evolution Reaction
HRTEM	High-Resolution Transmission Electron Microscopy
i-CRIM	i-Center for Research and Instrumentation Management
ID	Inner Diameter
IEA	International Energy Agency

LDOS	Layer Density of States
LSV	Linear Sweep Voltammetry
NHE	Normal Hydrogen Electrode
OD	Outer Diameter
OER	Oxygen Evolution Reaction
PBE	Perdew-Burke-Enzerhof
PC	Photocatalytic
PEC	Photoelectrochemical
RE	Reference electrode
rGO	Reduced Graphene Oxide
RHE	Reversible Hydrogen Electrode
SAED	Selected Area Electron Diffraction
SCE	Saturated Calomel Electrode
SCF	Self-Consistent Field
SDG	Sustainable Development Goals
SEM	Scanning Electron Microscope
SLG	Single Layer Graphene
SMR	Steam Methane Reforming
STATE	Simulation Tool for Atom Technology
STC	Solar Thermochemical
STH	Solar-to-Hydrogen
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TMDC	Transition Metal Dichalcogenide
UKM	Universiti Kebangsaan Malaysia
UV-Vis	Ultraviolet-Visible
VB	Valence band
vdW	van der Waals
WE	Working electrode

XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction



LIST OF NOMENCLATURES

μA	microampere
μmol	micromole
A	Ampere
Ag	Silver
Ag/AgCl	Silver/Silver Chloride
Ar	Argon
Au	Gold
BiVO_4	Bismuth vanadate
C	Carbon
CdS	Cadmium sulfide
CH_4	Methane
cm	centimetre
cm^2	centimetre square
cm^3	centimetre cubic
Co	Cobalt
CO_2	Carbon dioxide
Cu	Copper
Cu_2O	Copper (II) oxide
DI	Deionized
DMPDA	2,2'-dimethyl-4,4'-biphenyldiamine
EA	Electron Affinity
Fe	Iron
Fe_2O_3	Iron (III) oxide
GaON	Gallium oxynitride
$\text{g-C}_3\text{N}_4$	Graphitic carbon nitride
H	Hydrogen
H_2	Hydrogen gas

H ₂ O	Water
H ₂ SO ₄	Sulfuric acid
HCl	Hydrochloric acid
InP	Indium phosphide
KCl	Potassium chloride
kHz	kilohertz
kJ	kilojoule
KOH	Potassium hydroxide
kV	kilovolt
L	Litre
M	Molar
m ²	metre square
mA	milliampere
MDA	4,40-diaminodiphenylmethane
min	minute
mL	millilitre
mm	millimetre
mmol	millimole
mol	mole
MoS ₂	Molybdenum disulfide
mV	millivolt
mW	milliwatt
N	Nitrogen
NaNO ₃	Sodium nitrate
Na ₂ S	Sodium sulfide
Na ₂ SO ₃	Sodium sulfite
Na ₂ SO ₄	Sodium sulfate
NaOH	Sodium hydroxide
Ni	Nickel

Ni(OH)_2	Nickel (II) hydroxide
NiO	Nickel (II) oxide
nm	nanometre
O	Oxygen
O_2	Oxygen gas
OH^-	Hydroxide ion
Pd	Palladium
Pt	Platinum
R_{ct}	Charge transfer resistance
rpm	rotation per minute
R_{y}	Rydberg
sccm	standard cubic centimetres
Si	Silicon
TiO_2	Titanium dioxide
WO_3	Tungsten trioxide
WS_2	Tungsten disulfide
Xe	Xenon
ZIF-8	Zeolitic Imidazolate Framework-8
Zn	Zinc
$\text{Zn(NO}_3)_3 \cdot 6\text{H}_2\text{O}$	Zinc nitrate hexahydrate
Zn(OH)_2	Zinc hydroxide
ZnCo_2O_4	Zinc cobalt oxide
ZnO	Zinc oxide

LIST OF SYMBOLS

$^{\circ}\text{C}$	Degree Celsius
A	Area of the photoelectrode
$\text{\AA}$	Angstrom
C	Coulomb
ΔG	Gibbs free energy
d_z	Interfacial distance in z-direction
e	Electron charge
ε	Dielectric constant
e^-	electron
E_b	Binding energy
$E_{b/n}$	Binding energy per carbon atom
E_f	Fermi level
E_g	Band gap
E_{graphene}	Total energy of graphene
E_{int}	Interaction energy
E_{Ni}	Total energy of Ni
eV	electron Volt
E_{ZnO}	Total energy of ZnO
F	Faraday constant
g	gram
G	Graphene
h	height
h^+	hole
$h\nu$	Incidence photon energy
I	Current
IP	Ionization potential
J_{ph}	Photocurrent density

λ	Wavelength
N_a	Electron acceptor
N_d	Electron donor
$\eta_{\text{experiment}}$	Molar flowrate from experimental measurements
$\eta_{\text{theoretical}}$	Molar flowrate from theoretical
P_{in}	Light intensity
P_{light}	Incident light intensity
Q	Total charge
r_{H_2}	Hydrogen production rate
s	second
$STH_{100\%}$	Solar-to-Hydrogen at FE of 100%
STH_{actual}	Actual Solar-to-Hydrogen
t	Reaction time
V	Voltage
ν	Frequency
$V_{\text{Ag/AgCl}}$	Voltage measured relative to the Ag/AgCl reference electrode
V_{app}	Applied potential
vdW_{graphene}	van der Waals correction of graphene
vdW_{Ni}	van der Waals correction of Ni
vdW_{ZnO}	van der Waals correction of ZnO
V_{O}	Oxygen vacancies
V_{rev}^0	Standard reversible potential for water splitting
V_{RHE}	Voltage measured relative to the RHE reference electrode
V_{Zn}	Zinc vacancies
X	Electronegativity
z_1	Distance between the first layer of ZnO and the graphene layer
z_2	Distance between the graphene layer and the topmost Ni layer
Zn_i	Zinc interstitial

α	Optical absorption coefficient
ε_0	Permittivity of free space
θ	Theta
$\rho_{graphene}$	Charge density of graphene
ρ_{Ni}	Charge density of Ni
ρ_{ZnO}	Charge density of ZnO
Ω	ohm



CHAPTER I

INTRODUCTION

1.1 RESEARCH BACKGROUND

Global population growth, together with ongoing economic expansion, has led to a sharp increase in energy demand across multiple sectors. The International Energy Agency (IEA) reported that global energy demand in 2024 increased by 2.2%, remarkably higher than the annual average recorded between 2013 and 2023, which is around 1.3% (IEA 2025). This trend shows that energy demand and consumption are rising, exceeding the average growth rate observed over the past decade. Since fossil fuels remain the primary source of energy, this situation places heavy pressure on limited energy resources and contributes significantly to greenhouse gas (GHG) emissions, primarily carbon dioxide (CO₂) which accelerate global warming (Kindra et al. 2023; Rampai et al. 2024).

Although the impact of these issues is widely known, fossil fuel consumption continues to rise annually, leading to severe climate change impacts such as flooding, drought, glacier melting, rising sea level and others. In addition, CO₂ emissions from the energy sector are predicted to increase from 50% in 2030 to 80% in 2050 (IEA 2009). Because of this, the environmental challenges driven by fossil fuels have become a major concern for nations worldwide. To overcome these challenges and support the global transition toward net-zero emissions by 2050, it is essential to develop sustainable, efficient, and clean energy solutions. These pathways demonstrate strong alignment with the United Nations Sustainable Development Goals (SDGs), particularly SDG 7 (affordable and clean energy) and SDG 13 (climate action), by advancing toward low-emission energy systems and reinforcing global sustainability frameworks through reliance on renewable resources (Athia et al. 2024).

This transition requires a comprehensive strategy that involves not only the large-scale expansion of renewable energy but also the integration of versatile alternative clean energy carriers. Among these, hydrogen (H_2) is notably attractive as it is the most abundant element in the universe, possesses the highest energy content of any fuel, is non-toxic, reliable and offers a sustainable and environmentally friendly energy option (Fernández-Arias et al. 2024; Sun et al. 2025). Nevertheless, despite its cosmic abundance, the actual amount of H_2 as a pure element exists in the Earth's atmosphere is very small, around 0.5 to 1 part per million. This is because H_2 is highly reactive and readily bonds with other elements, most commonly with oxygen (O) in water (H_2O) molecules (Rampai et al. 2024).

Currently, H_2 can be produced using both non-renewable (such as natural gas, coal, and nuclear power) and renewable energy sources (including hydro, wind, biomass, geothermal, and solar energy) (Mehmood et al. 2024). It is commonly classified using a “color-code” system based on energy source and method used, which serves as a quick indicator of the resulting hydrogen's environmental impact and sustainability (Fernández-Arias et al. 2024; Incer-Valverde et al. 2023). At present, the majority of H_2 produced globally is Grey H_2 , which is primarily derived from natural gas using Steam Methane Reforming (SMR). This process releases significant amounts of CO_2 directly into the atmosphere, making it the least sustainable option.

To address the climate impact of fossil fuels derived H_2 , Blue H_2 is produced using similar methods but incorporates Carbon, Capture, Utilization and Storage (CCUS) technology to capture and store CO_2 emissions, offering a lower-carbon transitional pathway. Turquoise H_2 represents an emerging category produced by methane (CH_4) pyrolysis, a process that splits CH_4 into H_2 and solid carbon. This approach can achieve low emissions if powered by renewable energy and if the resulting solid carbon is permanently stored and utilized. Meanwhile, Pink H_2 is produced through electrolysis powered by nuclear energy, which is also a very low-carbon process. However, debates are ongoing over nuclear waste disposal.

Yellow H_2 is produced via electrolysis that utilizes electricity from a mixed-source power grid, resulting in an emission profile that varies depending on the local

energy mix. In contrast, Green H₂ is considered the most environmentally sustainable and desirable form. It is produced through the electrolysis of H₂O powered exclusively by renewable energy sources, such as wind and solar energy. This process produces virtually zero GHG emissions, aligning closely with global decarbonization goals. Among these, Green H₂ is usually produced using solar energy, which enables H₂O splitting through three distinct routes: (1) solar thermochemical (STC), which utilizes high-temperature to convert solar radiation into heat energy that drives water splitting, (2) photocatalytic (PC), which suspended semiconductor particles or powders that directly use solar energy to split H₂O molecules, and (3) photoelectrochemical (PEC), which employ semiconductor thin films as photoelectrodes to generate H₂ and O₂ (Qureshi & Tahir 2024; TuluHong et al. 2024).

Among these methods, PEC systems are considered the most promising for practical solar H₂ production, as both STC and PC systems continue to encounter significant challenges related to inefficient H₂ production, limited durability and poor long-term operational stability. A distinct advantage of PEC systems is their ability to drive water splitting utilizing primarily solar energy to produce H₂. This process relies on a semiconductor photoelectrode as the photoactive material to absorb light and perform hydrogen evolution reaction (HER) or oxygen evolution reaction (OER), as well as a counter electrode (CE) to drive the other half reaction (Chen et al. 2020). The pioneering study by Fujishima and Honda in 1972, using titanium dioxide (TiO₂), established the fundamental requirements for efficient photoelectrode: effective light absorption, efficient charge separation and transport, and chemical stability in aqueous environments (Fujishima & Honda 1972).

Building upon the foundation work with TiO₂, extensive research has focused on exploring alternative metal oxide semiconductors that can fulfill water splitting criteria. Among them, zinc oxide (ZnO) has emerged as a highly attractive photoanode material for PEC water splitting due to its non-toxic, unique physicochemical properties, and high thermal and mechanical stability (Raha & Ahmaruzzaman 2022). However, the PEC performance of ZnO is hindered by its wide band gap (E_g) (3.37 eV), which limits its light absorption and leads to a high recombination rate of photogenerated electron-hole ($e^- - h^+$) pairs. To mitigate these drawbacks, coupling

ZnO with graphene has proven to be an effective strategy. Graphene has zero band gaps, exceptional electrical conductivity, and fast charge carrier transport, acts as a conductive bridge to facilitate charge transfer. Nevertheless, the physical integration of graphene is complicated by its two-dimensional (2D) nature, making it easy to aggregate, folding, or wrinkling induced by strong van der Waals (vdW) forces. To resolve this structural instability, a highly conductive, three-dimensional (3D) substrate like nickel foam (Ni-foam) is required. The interconnected, porous structure of Ni-foam provides a high surface area that prevents graphene restacking, while its strong adsorption capability for graphene ensures a highly stable and efficient photoanode structure.

1.2 MOTIVATION

The pursuit of sustainable energy solutions is important in addressing the growing global energy demand while mitigating the effects of climate change. Within this context, PEC water splitting, which directly harnesses solar energy to produce H₂ fuel, presents a particularly promising approach for next-generation energy production. In this system, the photocatalyst serves as the critical functional component that determines the charge generation, separation, and the subsequent oxidation or reduction reactions of H₂O. However, the large scale and practical implementation of PEC technology remain significantly hindered by the critical limitations of current semiconductor photocatalysts, which suffer from low solar-to-hydrogen (STH) conversion efficiency, poor stability, and limited light absorption. This thesis is therefore motivated by the urgent need to develop an advanced photoelectrode materials that can overcome these obstacles and unlock the full potential of solar H₂ generation.

1.3 PROBLEM STATEMENT

To address the pressing global energy demands, PEC water splitting holds a significant promise as a sustainable pathway for H₂ production. However, the semiconductor materials used as photoelectrode for PEC suffer from $e^- - h^+$ recombination and poor stability in electrolyte (Mahmud et al. 2020). This will affect the long-term performance and reliability of the PEC systems. To overcome these challenges, the development of efficient photoelectrodes is crucial. Semiconductor materials, such as ZnO, play an

important role in PEC system. However, a significant drawback of ZnO is its ability to absorb only a small portion of the solar spectrum due to its wide band gap. In addition, ZnO is prone to photocorrosion in aqueous electrolytes, which affects the structural stability of the photoelectrode, thereby hindering its practical application as a photoelectrode in PEC systems (Mahala et al. 2019; Raza et al. 2016; Sushma & Girish Kumar 2017). This can result in a high recombination rate of $e^- - h^+$ pairs which limit photocatalytic performance and reduce the stability of the ZnO. Consequently, coupling ZnO with highly conductive graphene has been proposed as a promising solution to enhance electron transport and prevent recombination, as well as improve stability.

Nevertheless, practical implementation is severely hindered by graphene's issue towards aggregation, wrinkling, and folding due to strong vdW forces (Lin et al. 2018). This structural instability drastically reduces the active surface area and impedes charge transfer kinetics, leading to limited PEC performance and poor long-term durability. Therefore, a critical gap remains in developing a stable and efficient substrate engineering strategy that can simultaneously mitigate graphene aggregation, promote mass transport, enhance light absorption, and improve charge separation efficiency. Addressing these challenges is crucial for achieving robust, highly efficient PEC systems with long-term operational stability. Furthermore, the implementation of ZnO/graphene photoelectrodes is complicated by the limitations of current synthesis techniques. Existing common synthesis techniques such as sol-gel, electrochemical deposition, ball milling, etc often involve complex, energy-intensive, or multi-step processes, making it challenging to achieve a uniform and controllable growth of both ZnO and graphene, as well as a stable and stronger interfacial contact between the ZnO and the graphene component (Gao et al. 2021). These difficulties frequently result in poor ZnO crystallinity, defect formation in the ZnO structures, weak adhesion to the conductive metal substrate, and non-uniform graphene distribution throughout the photoelectrode layer. Although fluorine-doped tin oxide (FTO) is widely used as a conventional substrate for photoelectrodes due to its transparency and conductivity, its planar structure provides limited surface area for active material loading and suffers from higher interfacial resistance. These limitations can hinder the current density and reduce the overall PEC performance. To overcome this, Ni-foam emerges as a superior substrate, providing a 3D interconnected conductive network that suppresses graphene

aggregation while ensuring robust interfacial contact with ZnO. The interconnected porous network of Ni-foam not only prevents graphene restacking but also provides a high surface area conductive substrate for efficient electrolyte pathway. Consequently, a critical gap remains in developing an effective synthesis strategy that can simultaneously mitigate graphene aggregation and facilitate the growth of a structurally robust, highly interconnected ZnO/graphene structure directly on a Ni-foam conductive metal substrate for superior PEC performance.

Although integrating graphene into ZnO effectively suppresses $e^- - h^+$ recombination, optimizing the efficient interfacial contact for charge transfer within the ZnO/graphene as photoelectrode remains a significant challenge for achieving high photocurrent densities (Su et al. 2018). This structural limitation is further compounded by a significant knowledge gap regarding the H_2 production yields of PEC systems, which hidden the economic viability required for large-scale commercialization. Until now, the current understanding of the synergistic effect between ZnO/graphene morphology and H_2 evolution rates remains poorly understood, hindering the development of efficient pathway for efficient PEC water splitting.

Beyond the challenges of physical synthesis and substrate selection, the fundamental understanding of charge carrier behaviour in ZnO/graphene composites remains largely dependent on experimental measurements. While these measurements yield excellent results like overall photocurrent, it provides limited atomistic insight into the underlying charge transfer processes. Consequently, a significant theoretical gap remains in the ability to accurately modelling and predicting interfacial charge transfer mechanisms (Darma et al. 2015; Fathzadeh et al. 2020). This includes determining the precise band alignment at the ZnO/graphene heterojunction, identifying the limiting pathway of $e^- - h^+$ separation and transfer, and understanding the impact of structural defects or aggregation influence electronic efficiency (Geng et al. 2013). Notably, while existing computational studies focused on ZnO/graphene or graphene/Ni interfaces, the combination of ZnO/graphene/Ni structure remains largely unexplored, especially on how the underlying metal substrate actively modulates these electronic interactions. Without a robust theoretical framework, researchers are constrained by the lack of predictive tools required to rationally design highly efficient photoelectrodes by

tuning the electronic properties at the atomic level, thereby hindering the iterative process of experimental optimization.

Therefore, based on the stated problem statements and gaps, the research questions in this study can be summarized as follows:

- i. How does the control of synthesis parameters and selection of proper conductive metal substrate influence the graphene structural quality, morphology, layer integrity, charge transfer efficiency, and PEC performance of the photoelectrode?
- ii. What is the relationship between the ZnO synthesis conditions and the resulting physicochemical properties (e.g., crystallinity, interfacial contact) of the final ZnO/graphene-based photoelectrode?
- iii. What is the optimal photoelectrode structure required to achieve maximum PEC activity, stability, and enhanced H₂ production rate under solar irradiation?
- iv. What are the fundamental charge transfer mechanisms and electronic band alignments at the ZnO/graphene interface, and how can these be accurately predicted?

1.4 RESEARCH OBJECTIVES

This research objectives of this study are as follows:

- i. To investigate the effect of chemical vapor deposition (CVD) parameters including annealing time, CH₄ flow rate, and growth time on the morphological and structural properties of graphene on Ni-based conductive metal substrate.
- ii. To study the structure-property relationship of hydrothermally grown ZnO nanostructures on a graphene/Ni by correlating their physicochemical properties with PEC performance for enhanced solar-driven water splitting.
- iii. To evaluate and correlate the PEC activity and H₂ production rate of ZnO/graphene/Ni photoelectrode.

- iv. To elucidate the charge transfer mechanism between ZnO and graphene/Ni as photoelectrode in the PEC using experimental and Density Functional Theory (DFT) study.

1.5 SIGNIFICANCE OF THE STUDY

The development of efficient, durable, and economically viable photoelectrodes is a fundamental requirement for the transition toward a sustainable hydrogen-based energy economy. This study presents a strategic contribution to PEC technology, with its primary novelty centered on the integration of graphene/Ni substrate as a foundational architecture for ZnO growth. The significance of this work lies in elucidating how the graphene/Ni interface significantly influences the PEC properties of the ZnO as a photoelectrode. Specifically, the introduction of the graphene/Ni substrate effectively broadens the light absorption range, optimizes the E_g , and significantly enhances the overall PEC performance of the resulting ZnO/graphene/Ni photoelectrode. The main technical contribution of this research is the demonstration of a reduced onset potential for the water splitting reaction. By lowering the potential required to initiate the reaction, the energy input is minimized, thereby reducing the operational power demand associated with H_2 production. Furthermore, the impact of this study is strengthened by an atomic-level investigation using DFT. By bridging the gap between experimental observations with theoretical simulations, this study provides a fundamental understanding into interfacial charge transfer mechanisms that influence PEC performance at the atomic level. Overall, the results demonstrate that the optimized ZnO/graphene/Ni photoelectrode successfully overcomes the major drawbacks of rapid $e^- - h^+$ pair recombination. By facilitating enhanced interfacial charge transfer, the synergistic interactions among ZnO, graphene, and Ni significantly improve the overall efficiency of H_2 production. This enhancement is important because H_2 is recognized as a clean, zero-emission energy source with strong potential to replace conventional fossil fuels. Beyond the laboratory scale, this research holds significant global implications by directly aligning with the SDG 7 and SDG 13. By establishing a systematic framework for tailoring the morphological and structural properties of photoelectrodes using earth-abundant materials, this study provides a critical roadmap

for developing high-efficiency, cost-effective H₂ production technologies to meet future industrial energy demands while mitigating environmental impacts.

1.6 RESEARCH SCOPE

This study is designed to synthesis, characterize, and test a novel ZnO/graphene/Ni photoelectrode for enhanced PEC H₂ production.

i. Substrate selection and optimization

A preliminary study will compare the morphological and PEC performance of Ni-based conductive metal substrates (foil and foam) to identify the most suitable substrate for photoelectrode development.

ii. Graphene synthesis and characterization

Graphene will be grown directly on the optimized Ni substrate using the CVD method. Main CVD parameters (annealing time, CH₄ flow rate, and growth time) will be systematically tuned to achieve high-quality graphene formation. The resulting graphene/Ni composite will be characterized to confirm the successful growth of graphene, evaluate its structural and morphological properties, and its initial PEC activity.

iii. ZnO/graphene/Ni photoelectrode preparation

The graphene/Ni substrate will be decorated with ZnO using a hydrothermal method. The reaction temperature will be the primary variable tuned to control the physicochemical properties (e.g., crystallinity, morphology, chemical bonding) of the final ZnO/graphene/Ni photoelectrode.

iv. Photoelectrochemical performance evaluation

The synthesized photoelectrodes will be systematically tested to determine PEC activity and H₂ production rate. This includes standard electrochemical techniques such as Linear Sweep Voltammetry (LSV), Electrochemical Impedance Spectroscopy (EIS), and Chronoamperometry (CA), conducted under 0.5 M sodium sulfite (Na₂SO₃) electrolyte conditions to elucidate charge transfer behavior and PEC activity of the developed photoelectrode.

v. Mechanism and theoretical elucidation

The study will conclude by elucidating the charge transfer mechanism of the optimized photoelectrode. This will involve two approaches: experimental analysis (Ultraviolet-visible; UV-vis, LSV, CA, EIS, Mott-Schottky, Gas Chromatography; GC) of the electronic properties and DFT calculations to accurately model the band alignment and interfacial charge interactions at the ZnO/graphene/Ni heterojunction.

1.7 THESIS ARRANGEMENT

The thesis is systematically organized into five main chapters to provide a comprehensive overview of the research. Chapter I, Introduction, establishes the global context of sustainable energy and PEC H₂ production, defines the research problem and existing knowledge gaps, and outlines the objective and scope of the study. Chapter II, Literature Review, provides a comprehensive and critical review of the state-of-the-art in PEC water splitting, covering fundamental mechanisms, current photoelectrode materials, advanced material design strategies, and the established experimental and theoretical frameworks for analyzing charge transfer mechanisms.

Chapter III, Methodology, also discussed the entire experimental and computational procedures, including materials selection and preparation (e.g., substrate selection, graphene and ZnO synthesis), along with detailed specifications of the characterization techniques used. This chapter also describes the computational approach (DFT modeling) employed for theoretical study. Chapter IV, Results and

Discussion, presents a detailed analysis of the research findings, systematically organized to address the research objectives. This includes the optimization of synthesis parameters, physicochemical characterization, and a critical evaluation of the PEC performance and H₂ production efficiency. Furthermore, this chapter also includes an in-depth discussion correlating experimental data with theoretical modeling to fully elucidate the charge transfer mechanism.

Finally, Chapter V, Conclusion and Future Work, summarizes the key findings and significant contribution of the research, highlighting how the designed ZnO/graphene/Ni structure effectively addressed the identified structural and electronic limitations. Besides, this chapter provides a detailed discussion on the limitations encountered and proposes specific directions for future research to extend the continuity of the observations, scale up the technology and further validate the long-term commercial viability of the material.

CHAPTER II

LITERATURE REVIEW

2.1 INTRODUCTION

The rapid development of modern society has increased global concerns regarding environmental pollution and limited energy availability, largely driven by the excessive consumption of fossil fuels. Consequently, the transition toward clean and renewable energy sources is critical to meet rising global energy demands while mitigating greenhouse gas (GHG) emissions. Among available resources, solar energy has attracted significant attention due to its abundance, sustainability, and environmental compatibility (Kumar et al. 2022; Su et al. 2018). However, for practical large-scale applications, solar energy must be converted into storable and transportable forms, such as chemical fuels, to overcome its intermittent nature (Ros et al. 2020).

Water splitting has emerged as a promising strategy for converting solar energy into hydrogen (H_2) fuel. By splitting water (H_2O) into its constituent elements like H_2 and oxygen (O_2), energy is captured and stored in the chemical bonds of H_2 (Kumar et al. 2022). This process essentially creates a closed-loop energy cycle in which the only byproduct of energy consumption is H_2O vapor, offering a sustainable alternative to fossil fuels. When the energy used to split the H_2O is derived from renewable sources such as sun or wind, the produced H_2 is referred to as Green H_2 , which strongly aligns global decarbonization and net-zero emissions goals (Qureshi & Tahir 2024; Tuluhong et al. 2024).

As mentioned in Section 1.1, Green H_2 can be achieved through three technological pathways, like STC, PC, and PEC. Figure 2.1 illustrated global research trend for research article related to these three technologies. It indicates a significant increase in activity within these fields, highlighting their potential as future energy

solutions from 2015 until 2025. Among them, PEC water splitting is widely considered the most promising technology because it integrates the high conversion efficiency of photovoltaic system with the low-cost potential of photocatalysis (Jian et al. 2018). Currently, the research efforts are shifting toward the development of efficient and robust photoelectrodes capable of enhancing charge separation, improving stability, and sustaining long-term operational durability.

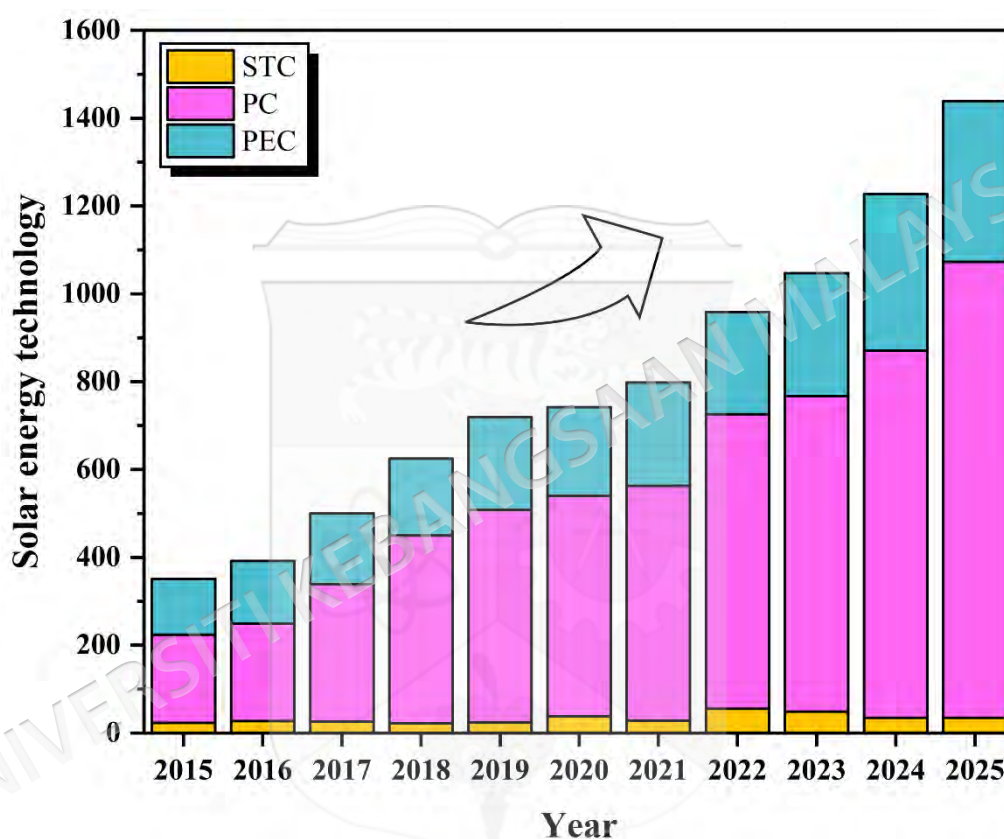


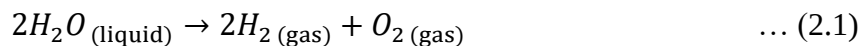
Figure 2.1 Scopus-based publication numbers for solar-driven H_2 production technologies from 2015 to 2025. Data retrieved using TITLE-ABS-KEY for “solar thermochemical water splitting for hydrogen production”, “photocatalytic water splitting for hydrogen production”, and “photoelectrochemical water splitting for hydrogen production”.

2.2 WORKING PRINCIPLES AND CONFIGURATIONS OF PHOTOELECTROCHEMICAL (PEC) CELLS

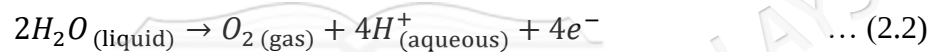
Photoelectrochemical (PEC) water splitting is a process to produce H_2 from H_2O using sunlight. This process is highly attractive because it directly converts solar energy into chemical energy, producing clean H_2 and O_2 , with the potential for low or no GHG emissions. The overall water splitting process is driven by two-half reactions: hydrogen

evolution reaction (HER) and oxygen evolution reaction (OER). This reaction requires a minimum thermodynamic energy input of $\Delta G = 273.15 \text{ kJ/mol}$ (corresponds to $\Delta E = +1.23 \text{ V}$). Furthermore, the reaction equation is depends on the experimental conditions (Qureshi & Tahir 2024), where the equations are typically written as follows:

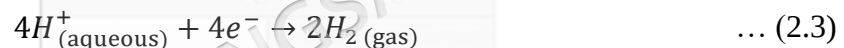
The water splitting reaction:



Anode (oxidation):



Cathode (reduction):



To practically achieve PEC reactions, a PEC cell is required. Generally, it consists of several essential components: (i) electrolyte, (ii) counter electrode (CE), (iii) reference electrode (RE), and (iv) working electrode (WE) (Minggu et al. 2010; Vilanova et al. 2024). Each component performs a specific role that governs overall PEC efficiency. The electrolyte provides ionic conductivity and serves as the medium for redox reactions occurring at the photoelectrode-electrolyte interface. It can be classified as acidic (sulfuric acid; H_2SO_4 , hydrochloric acid; HCl), neutral (sodium sulfate; Na_2SO_4 , sodium sulfite; Na_2SO_3), or basic (sodium hydroxide; $NaOH$, potassium hydroxide; KOH) electrolyte (Guo et al. 2018; Kaur et al. 2021; Rosman et al. 2021; Salehmin et al. 2018). The selection of an appropriate electrolyte must consider its chemical compatibility with the photoelectrode to prevent corrosion or material degradation during experiments (He et al. 2024).

In addition, a complete PEC system requires not only the cell but also the light source, potentiostat, monitor, and connecting wire. The light source serves as the main energy input for PEC water splitting reaction, providing the photons that generate

$e^- - h^+$ pairs within the photoelectrode. In standard PEC setups, a solar simulator equipped with a xenon (Xe) lamp is commonly used to replicate the solar spectrum under AM 1.5G filter, corresponding to an intensity of 100 mW/cm^2 (Arifin et al. 2021). This standardized setup allows for consistent performance comparison among different photoelectrode materials under stimulated sunlight. Also, the CE facilitates the complementary half-reaction to maintain charge balance in the PEC system. For n-type semiconductors, platinum (Pt) foils, mesh, or wire are typically used due to its high catalytic activity toward the HER, where H^+ ions are reduced to H_2 . However, Pt as CE is less effective for p-type semiconductors because of its poor catalytic performance toward the OER, where H_2O is oxidized to produce H^+ and O_2 . In such cases, conductive metal oxides such as ruthenium (IV) oxide (Ru_2O) or iridium (IV) oxide (IrO_2) are preferred candidates, as it is effectively lower the overpotential required for OER and improve overall PEC performance.

Meanwhile, RE provides a stable potential reference for measuring the WE potential during PEC characterization. This ensures accurate determination of the applied bias and enables reliable comparison of PEC performance between studies. Commonly used RE includes the silver/silver chloride (Ag/AgCl) in 3.0 M potassium chloride (KCl), the saturated calomel electrode (SCE), and the reversible hydrogen electrode (RHE). Among these, the RHE is most widely used in PEC water splitting because it offers a pH-independent potential scale, allowing direct correlation with the thermodynamic potentials of the HER and OER. However, when Ag/AgCl or SCE electrodes are used, the measured potentials must be converted to the RHE scale using standard conversion equations to ensure consistency in data reporting. Proper selection and calibration of the RE are essential to minimize measurement errors and achieving reliable reproducibility in PEC analysis.

The WE are the main component of the PEC system, which incorporates photoactive material known as the photoelectrode. It can be categorized as a photoanode or photocathode, depending on the semiconductor type and the dominant charge carrier involved. The overall PEC performance is strongly influenced by the intrinsic properties of the photoelectrode, such as E_g , band edge alignment, charge carrier transport, surface morphology, and photocatalytic activity (Ros et al. 2020). To enhance the activity and

stability of the WE, various modification approaches have been developed, including heterojunction formation, co-catalyst integration, elemental doping, and surface engineering. These methods aim to promote charge separation and suppress recombination, and improve the overall PEC efficiency (Mohd Shah et al. 2021). The overall configuration and components of the PEC system are illustrated in Figure 2.2.

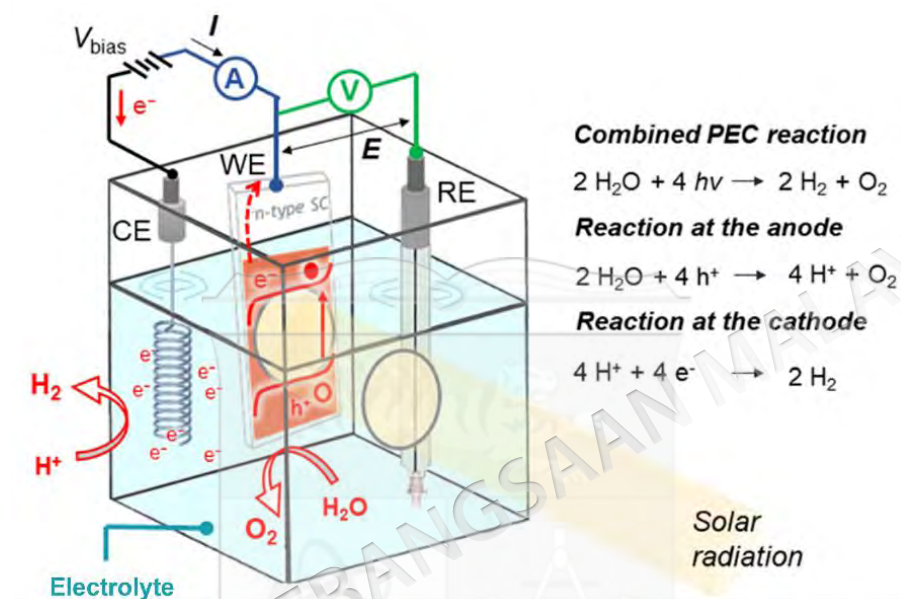


Figure 2.2 Illustration of the three-electrode PEC setup consisting of (i) n-type semiconductor WE, (ii) Pt coil CE, (iii) RE, and (iv) electrolyte. The circuit include electric bias (V_{bias}), current (I), and potential (E).

Source: Vilanova et al. (2024)

PEC water splitting offers a promising approach to sustainable H_2 production, using semiconductor materials to directly convert solar energy into chemical energy. The fundamental working principle relies on the photoelectrode absorbing light to generate $e^- - h^+$ pairs (Kumar et al. 2022). The overall STH efficiency depends on several factors, including the E_g , band edge positions relative to water redox potential, and the charge carrier transport. To improve overall efficiency of PEC systems, the cell can be designed with either single-absorber or tandem configurations (Liu et al. 2022; Qureshi & Tahir 2024). Each configuration offers different working mechanisms that influence light-harvesting capability and charge carrier dynamics. Hence, a clear understanding of these underlying mechanisms and design strategies is essential for the rational development of efficient and stable photoelectrodes for PEC water splitting.

2.2.1 Fundamental working principle

At the heart of the PEC is the photoelectrode, which usually consists of semiconductor materials that are capable to drive the water splitting reaction. As illustrated in Figure 2.3, the PEC process can be divided into four fundamental steps: (1) light absorption: incoming photons create an $e^- - h^+$ pair, (2) $e^- - h^+$ generation (the creation of the excited electron), (3) charge separation and transport (the internal electric field separates the charge carriers), and (4) redox reactions at the surface of the photoelectrode: the separated charges migrate to the surface to drive the HER and OER (Kindra et al. 2023; Mohd Shah et al. 2021; Tuluhong et al. 2024). The success of this fundamental step is critically dependent on the electronic and structural properties of the photoelectrode. This highlights why selecting and designing the suitable photoelectrode material is crucial, as enhanced efficiency is necessary to fully realize the potential of PEC water splitting.

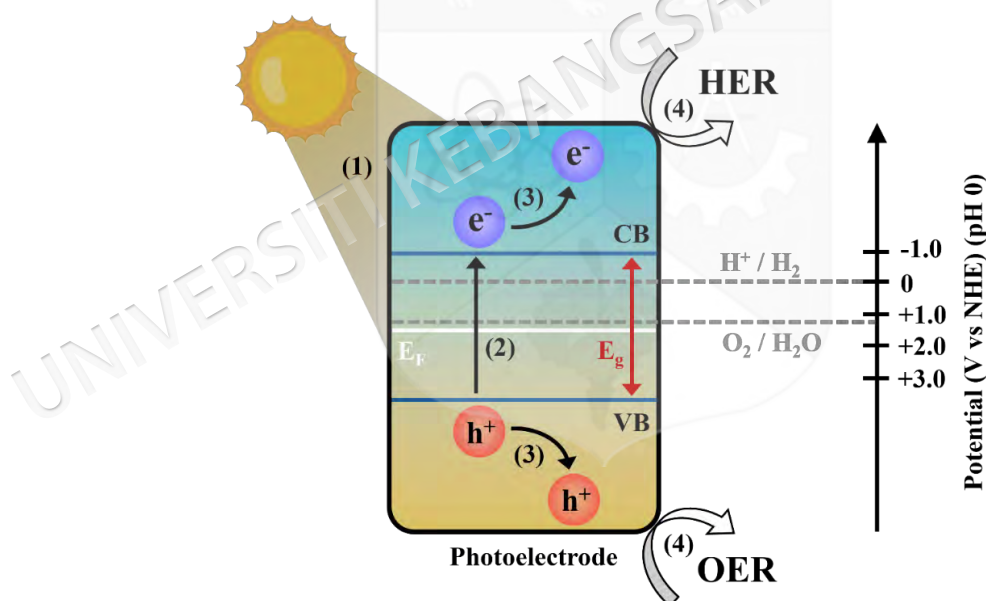


Figure 2.3 Illustration of the fundamental steps in PEC water splitting and the energy band alignment required to the H₂O redox potentials.

Subsequently, to meet the thermodynamic requirements for overall water splitting, the photoelectrode must fulfil two important electronic criteria: (1) the E_g of the photoelectrode should be at least or higher than 1.23 eV, and (2) it must have suitable band edge alignment, where the valence band (VB) and the conduction band (CB) positions straddle the redox potential of H₂O (Ager et al. 2015; Kumar et al. 2022; Li et

al. 2020). In other words, the VB minimum must be located below the OER potential, and the CB minimum must be located above the HER potential (Figure 2.3). In addition, the Fermi level (E_f) should be located near to the midpoint of the E_g , ensuring an equal number of photogenerated electrons and holes (Qureshi & Tahir 2024). While these electronic requirements determined the fundamental of water splitting, the efficient PEC technology also depends on how these photoelectrodes are integrated into the PEC configurations.

In a complete PEC system, the overall water splitting reaction involves two complementary half-reactions occurring at the photocathode (p-type) and photoanode (n-type), as shown in Figure 2.4 (Jiang et al. 2017; Ke et al. 2021; Zhang & Yates 2012). The photocathode, typically consists of p-type semiconductor, drives the HER (Hou et al. 2024). Upon illumination, photogenerated electron (minority charge carriers) move toward the electrode surface to reduce H^+ into H_2 . Effective HER performance requires the CB edge of the photocathode to lie more negative than the HER potential, providing sufficient driving force for proton reduction (Hamdani & Bhaskarwar 2021). When the p-type semiconductor contacts the electrolyte, downward band bending forms at the photoelectrode-electrolyte interface, promoting electron migration toward the surface and suppressing charge recombination, which enhance HER efficiency (Alfaifi et al. 2018; Jiang et al. 2017; Ke et al. 2021; Zhang & Yates 2012).

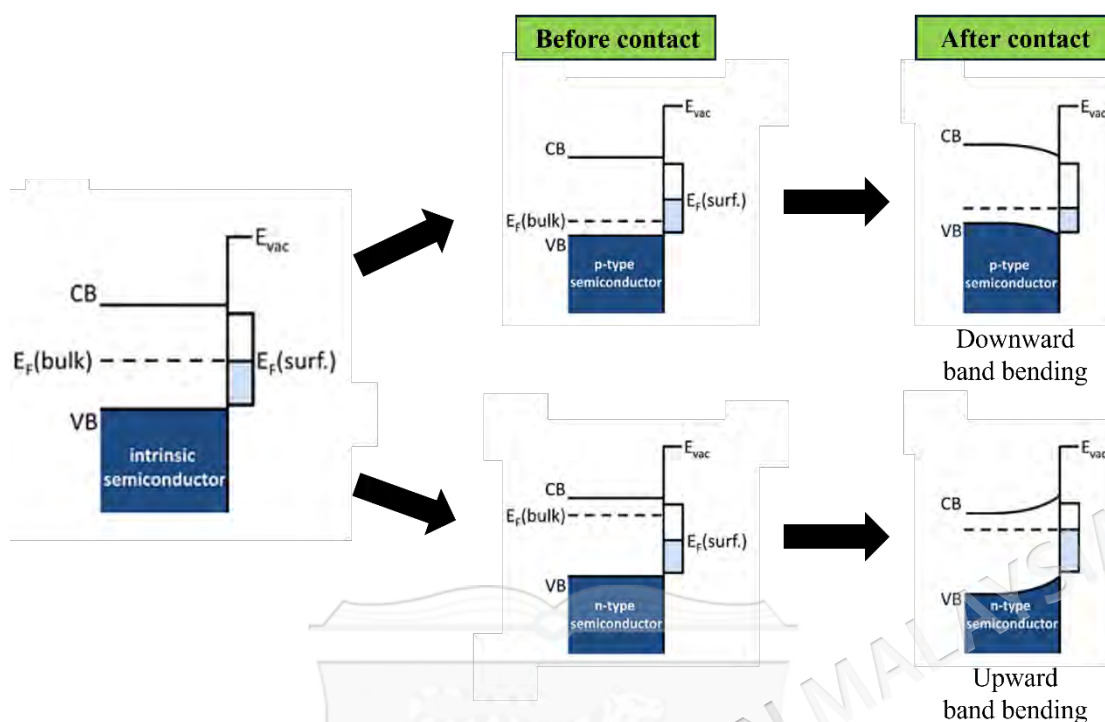


Figure 2.4 Band alignment of p-type and n-type semiconductors before and after contact, showing the Fermi level (E_f) alignment, band bending, and the vacuum energy (E_{vac}).

Source: Jiang et al. (2017) and Zhang & Yates (2012)

In contrast, the photoanode, composed of n-type semiconductor materials, facilitates the OER (Hou et al. 2024). Upon illumination, photons with sufficient energy excite electron from the VB to the CB, generating $e^- - h^+$ pairs. The photogenerated hole (minority charge carriers) migrate to the surface to oxidize H_2O into O_2 , while the excited electrons are transferred through the external circuit. When the n-type semiconductor contacts the electrolyte, upward band bending occurs at the photoelectrode-electrolyte interface, which drives hole towards the surface and electron toward the bulk region, thereby promoting charge separation (Alfaifi et al. 2018; Jiang et al. 2017; Ke et al. 2021; Ros et al. 2020; Zhang & Yates 2012). For efficient photoanode performance, a suitable E_g for visible-light absorption, favourable band alignment, high carrier mobility, and strong resistance to photocorrosion are essential. Overall, the performance of the photoelectrode depends on the configuration of the PEC cell such as single-absorber and tandem, which will be explained in the next section.

2.2.2 PEC configurations

a. Single-absorber configuration

One of the most widely studied PEC cell configurations is the single-absorber system, where only one of the two electrodes is photoactive material (either a photocathode or a photoanode), while the other electrode is a metal-based material such as Pt (Ahmed & Dincer 2019; Jiang et al. 2017). The photoactive electrode is needed to absorb light with sufficient energy to generate charge carriers within the bulk material. For a p-type photocathode configuration, the photogenerated electrons participate in the reduction of H^+ to produce H_2 at the surface of the semiconductor, while the corresponding oxidation reaction occurs at the CE. In contrast, a n-type photoanode configuration, the photoanode absorbs sunlight to excite electron from the VB to the CB, producing $e^- - h^+$ pairs. Then, the photogenerated holes stay at the semiconductor surface to oxidize H_2O into O_2 , whereas the excited electron are transferred through the external circuit to the CE, where HER occurs (Ishaq et al. 2021; Ma et al. 2020).

A schematic illustration of the single-absorber PEC configuration is shown in Figure 2.5. Although the single-absorber PEC designs are simple and easy to fabricate, but the overall STH efficiency is often limited (less than 1%) by the light absorption and photovoltage generation that requires an external bias. Therefore, optimizing band-edge positions and improving material stability are essential to enhance performance (Hamdani & Bhaskarwar 2021; Ke et al. 2021; Lyu et al. 2025). To address these limitations, advanced structural configurations have shifted toward utilizing highly porous 3D substrates as templates. The porous architecture provides a larger surface area for catalyst loading, shortens charge carrier diffusion pathways to minimize recombination, improve stability, and enhance light harvesting through multiple internal scattering effects (Anuar et al. 2024; Chaudhari et al. 2017). These advantages contribute significantly to improving the PEC performance of single-absorber configuration. Nevertheless, the performance of single-absorber configurations remains fundamentally constrained by their limited light-absorption range and photovoltage generation. This challenge has driven the development of tandem configurations, which combine multiple light absorber materials with complementary band gaps to broaden light absorption and generate significantly higher photovoltage output.

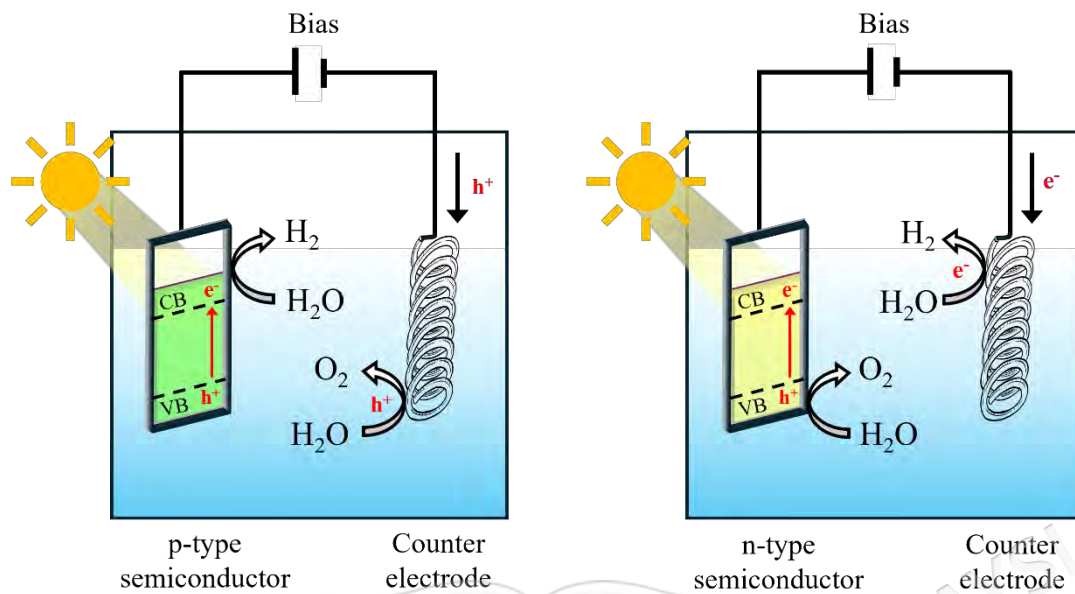


Figure 2.5 Schematic representation of a single-absorber PEC cell configuration.

Source: Ma et al. (2020)

b. Tandem configuration

As mentioned in (a), although single-absorber PEC designs are simple and easy to fabricate, their overall STH efficiency is often limited to less than 1%. This low efficiency is caused by restricted light absorption and insufficient photovoltage generation, which requires the use of an external bias. Hence, to overcome this disadvantage, the tandem PEC configuration has been developed. This configuration combines two semiconductor electrodes with different E_f (p-type photocathode and n-type photoanode) in a single PEC cell (Ke et al. 2021; Lyu et al. 2025). Both light-absorbing materials work together to drive the overall water splitting reaction efficiently without the need for an external bias. For efficient charge transfer, the CB minimum of the n-type photoanode should be more negative than the VB minimum of the p-type photocathode. In other words, a wide E_g semiconductor is positioned in front to absorb high-energy photons to drive the OER, allowing lower-energy photons to pass through and be absorbed by a narrower E_g semiconductor to drive the HER (Ahmed & Dincer 2019; Jiang et al. 2017). Commonly referred to as a “Z-scheme” PEC system, this configuration effectively broadens the solar spectrum utilization, allowing each photoelectrodes to operate closer to its optimal E_g (Hamdani & Bhaskarwar 2021).

As shown in Figure 2.6, tandem PEC systems can be arranged either in series (each photoelectrode are placed side by side on a single transparent conducting substrate coated on both sides) or parallel configurations (two substrate are used and transparency is not required), depending on the optical and electrical properties between those two materials. This design enhances solar spectrum utilization by allowing each photoelectrode to absorb light near its optimal E_g , thereby improving overall energy conversion efficiency (Jiang et al. 2017). The major advantage of the tandem configuration lies in its ability to generate a higher photogenerated voltage, as the combined potential difference from both photoelectrodes exceeds the thermodynamic requirement of 1.23 eV for overall water splitting (Alfaifi et al. 2018). This feature allows unassisted (bias-free) working conditions and enhances the overall STH efficiency. Various research has shown that the primary bottleneck in these configurations is the sluggish kinetics and high overpotential of the four-electron OER at the photoanode (Li et al. 2022). Therefore, the development of photoelectrode materials, especially photoanode are crucial.

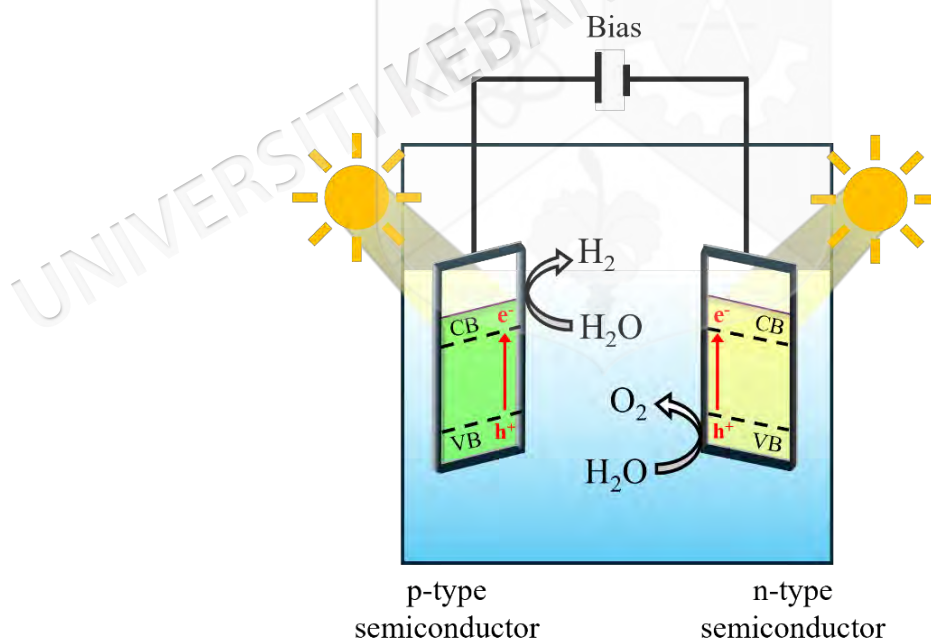


Figure 2.6 Schematic representation of a tandem PEC cell configuration.

Source: Ma et al. (2020)

Although the single photoanode configuration requires external bias and is not intended for large-scale practical hydrogen production due to the consumption of sacrificial agents, it provides important fundamental insights into the role of each component in enhancing PEC performance. Specifically, the utilization of a porous substrate offers significant advantages for electron transport and electrolyte accessibility. The understanding gained from this study ultimately serves as a valuable foundation for the future development for highly efficient single-absorber configuration.

2.2.3 Electrode components

As discussed earlier, in PEC water splitting, semiconductor materials are categorized as p-type or n-type, depending on their majority charge carriers and band structures. The p-type semiconductors such as Cu_2O , NiO , Si , InP have holes as the dominant charge carriers and act as photocathodes for the HER (Adris et al. 2024; Cheng et al. 2022; Ivanova et al. 2022; Salunkhe et al. 2020). In contrast, the n-type semiconductors like TiO_2 , iron (III) oxide (Fe_2O_3), ZnO have electrons as the majority carriers and are typically used as photoanodes to drive the OER (Ansari et al. 2019; Anuar et al. 2025; Yan et al. 2017). Despite their potential, the PEC performance of both semiconductor types is still limited by several critical challenges.

For instance, the p-type photocathodes are easy to oxidized and rapid degradation in aqueous environments (Ho et al. 2023; Sahu et al. 2020). Meanwhile, the n-type photoanodes generally suffer from wide E_g , which limit the ability of visible-light absorption, together with poor charge transport and photocorrosion issues (Tayebi et al. 2020; Warren et al. 2023). Moreover, the mismatched band alignment, short carrier lifetime, light absorption capability, and surface recombination further hinder the PEC efficiency (Aslam et al. 2024). Therefore, strategies such as band engineering, heterojunction design, and surface modification are essential to enhance light absorption, charge separation, and long-term stability of the photoelectrode.

a. Photocathodes

The photocathodes play a crucial role in driving the HER during PEC water splitting and are usually composed of a p-type semiconductor material. During illumination, the photocathodes absorb the incident photons with energy equal to or greater than its E_g , exciting the electron from the VB to the CB, and generating $e^- - h^+$ pairs. After that, the photogenerated electrons move toward the electrode-electrolyte interface, and H^+ is reduced from the electrolyte to produce H_2 . Meanwhile, the photogenerated holes move toward the back side of the photoelectrode and transported through the external circuit to the anode side and drives the OER (Dias & Mendes 2019).

For efficient photocathode, it should have sufficiently negative CB potential relative to the H^+/H_2 redox level (0 V vs. NHE at pH 0) to enable spontaneous H_2 generation. In addition, the photocathodes must have high charge carrier mobility, strong light absorption, chemical stability in aqueous media, and low overpotential for HER (Wang et al. 2024). However, the main challenges with photocathodes such as poor stability under illumination, surface corrosion, and fast charge recombination continue to limit the long-term PEC performance of photocathodes.

b. Photoanodes

Photoanodes, which is composed of the n-type semiconductor materials, act as the main components in PEC water splitting systems for driving the OER. Upon illumination, it absorbs photons with energy equal to or greater than its E_g , excite the electron from the VB to the CB, and generating $e^- - h^+$ pairs. The photogenerated holes transport toward the photoelectrode-electrolyte interface, after that oxidized H_2O to produce O_2 . Meanwhile, the excited electron are transferred through the external circuit to the cathode side to drive HER (Abdullah et al. 2023; Dias & Mendes 2019).

An efficient photoanode should possess a VB potential that is sufficiently positive relative to the H_2O/O_2 redox potential (+1.23 V vs. NHE at pH 0) to drive OER (Qiu et al. 2019). Additionally, it should exhibit strong visible-light absorption, high charge carrier mobility, low recombination rate, and stable under oxidative conditions (Chen et al. 2025; Li et al. 2022). However, the photoanodes commonly suffer from

slow OER kinetics, surface recombination, and photocorrosion, which significantly limit the PEC performance and long-term stability.

2.3 PHOTOANODE MATERIALS FOR PEC WATER SPLITTING

Photoanode materials play a crucial role in determining the overall performance of PEC water splitting systems. As for the active sites of the OER, the photoanode is responsible for light absorption, generating charge carriers, and the oxidation of H_2O to produce O_2 . As mentioned, the photoanode must exhibit an appropriate E_g , suitable band alignment, strong light absorption capability, and high stability in aqueous environments to achieve high efficiency. A wide range of semiconductor materials, such as metal oxides, dichalcogenides, and sulphides have been explored as the photoanode. The following section highlights several promising photoanode materials that have been extensively studied for PEC water splitting applications.

2.3.1 Metal oxide based

Metal oxide semiconductors such as TiO_2 , Fe_2O_3 , and ZnO are among the most widely studied as the photoanodes for PEC water splitting. Their favorable electronic structures and excellent chemical stability make them highly attractive, but the challenges related to stability in aqueous solutions, limited light absorption, and charge recombination remain challenging. For instance, TiO_2 with an E_g of 3.0 – 3.2 eV, is one of the stable materials against photocorrosion and chemical corrosion as well as environmentally friendly. Nevertheless, its wide E_g restricts light absorption to the UV region, leading to low visible-light utilization (Arifin et al. 2021; Madhumitha et al. 2018). For instance, On the other hand, Fe_2O_3 with a narrower E_g of 2.0 – 2.2 eV, offers better visible-light absorption but suffers from a low diffusion length and poor conductivity, resulting in high charge recombination rates and reduced PEC efficiency (Mishra & Chun 2015).

Among these metal oxides, ZnO has also gained significant attention as photoanode materials. Other than having similar E_g to TiO_2 , ZnO is a non-toxic, offers high electron mobility, easy to synthesize into a variety of high surface area nanostructures and has suitable band edge positions for the OER (Arya et al. 2021; Güell

et al. 2023). However, its wide E_g (3.37 eV) limits light absorption where it is only absorbing UV light and prone to photocorrosion under illumination in aqueous solution (Folawewo & Bala 2022). In addition, ZnO nanostructures often suffer from agglomeration, which reduces the effective surface area and limits charge transport efficiency (Wahyuno et al. 2016). While these metal oxides demonstrate strong photochemical stability and good compatibility with PEC systems, their intrinsic limitations in light absorption and rapid $e^- - h^+$ recombination require further improvement through approaches such as doping, surface modification, or heterojunction engineering.

2.3.2 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDCs) such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) have emerged as promising materials for PEC water splitting due to their unique layered structures and tunable electronic properties. These 2D materials can exist in several structural phases, from different coordination environments of the transition of metal atoms. The most common structural phases are characterized by trigonal prismatic (2H) and octahedral (1T) coordination of metal atoms (Dias et al. 2018; Manzeli et al. 2017). TMDCs consist of covalently bonded chalcogen-metal-chalcogen (X-M-X) layers (where X = S, Se or Te and M = Mo or W) held together by weak VdW forces, which facilitate efficient charge transport and enable surface modification (Yunus et al. 2020).

Among TMDCs, MoS_2 is one of the most extensively studied, with an indirect E_g of about 1.2 eV (bulk form) and a direct E_g of 1.8 eV (monolayer form) (Dong et al. 2019; Li et al. 2015). It demonstrates high catalytic activity toward surface reactions. However, for the HER, only the edge sites of MoS_2 are catalytically active. This requires the controlled synthesis of MoS_2 layers with an abundant exposed edge sites to achieve high PEC performance. Similarly, WS_2 with a comparable E_g range of 1.3 – 2.1 eV, exhibits a less electronegative VB and cationic CB characteristics with high reducing activity, making it suitable for efficient OER (Chen et al. 2013; Vattikuti et al. 2016). The layered morphology of TMDCs provides more active sites and short charge diffusion paths, which promote effective charge separation and enhance surface

reactions kinetics (Rosman et al. 2018). However, their PEC performance remains limited by low photogenerated voltage and interlayer charge recombination. These challenges can be overcome through heterostructure formation, defect engineering, or surface engineering to improve light absorption and PEC performance.

2.3.3 Noble metals and alloys

Noble metals and their alloys, such as gold (Au), silver (Ag), Pt and palladium (Pd), are widely used as co-catalyst in PEC water splitting due to their excellent catalytic activity, high electrical conductivity, and chemical stability under aqueous and illuminated environments (Fageria et al. 2014; Wu et al. 2016). As co-catalyst, these metals provide high electron affinity and demonstrates the highest Schottky barrier at the metal-semiconductor interface for both the HER and the OER, thereby enhancing the overall reaction kinetics. In addition, noble metals such as Au and Ag exhibit strong surface plasmons resonance effects, which improve light absorption and promote hot-electron injection into the semiconductor, leading to increased photocurrent generation (Chibac-Scutaru et al. 2020; Güy & Özacar 2016; Zhang et al. 2020).

When combined as alloys or nanostructured composites, these metals can further improve charge transfer and increase interfacial stability. However, the scarcity and high cost of noble metals remain significant challenges for large-scale PEC applications (Fu et al. 2020). Therefore, current research effort focuses on reducing noble metal loading, developing alloyed nanostructures, or replacing them with earth-abundant alternatives such as transition metal oxides, sulfides, or phosphides, while maintaining high catalytic performance.

2.4 ZINC OXIDE (ZnO) AS A PHOTOANODE MATERIAL

In recent years, zinc oxide (ZnO) has gained significant attention as a photoanode material for PEC water splitting due to its favourable band-edge positions for driving the OER. In addition to having a E_g similar to TiO_2 , ZnO can also be easily synthesized into various high surface area nanostructures, which facilitate efficient charge transfer and improve light absorption (Mohan et al. 2020; Raizada et al. 2019). Owing to its abundance, non-toxicity, and environmentally friendly, ZnO has emerged as a

promising candidate for developing advanced photoanodes and exploring modification strategies at enhancing PEC and STH efficiency for sustainable H₂ production.

2.4.1 Properties and challenges of ZnO

ZnO is an n-type semiconductor that exhibits several promising properties for PEC water splitting applications. It is non-toxic and environmentally friendly, making it a sustainable alternative to other semiconductor materials. Aside from its environmental advantages, ZnO has well-aligned band edges suitable for OER, making it an excellent candidate as a photoanode (Chougale 2025; Kang et al. 2019). Its high electron mobility further enhances its performance by promoting efficient charge transfer and suppressing the recombination of photogenerated $e^- - h^+$ pairs. Furthermore, ZnO has tuneable morphology, as it can be easily synthesized into various high surface area nanostructures, such as nanorods, nanowires, nanoflower, and nanosheets, that significantly enhance light absorption and photocatalytic activity (Hezam et al. 2022; Ma et al. 2020). In addition, ZnO can exist in zinc-blende, rocksalt, and wurtzite phases. However, the hexagonal wurtzite structure (lattice constant of $a = 3.25 \text{ \AA}$, $c = 5.20 \text{ \AA}$) is the most common and stable form as photocatalysts (Mohd Adnan et al. 2016; Raizada et al. 2019).

Despite its advantages, ZnO suffers from several challenges as a photoanode material, as summarized in Figure 2.7. Its wide E_g restricts light absorption, especially to the UV region ($\lambda < 370 \text{ nm}$), which is less than 5% of the total solar spectrum (Beura & Thangadurai 2018; Folawewo & Bala 2022; Güler et al. 2023; Khan et al. 2018). This limitation results in very low STH efficiency. Furthermore, the wide E_g of ZnO contributes to a high recombination rate of photogenerated $e^- - h^+$ pairs, which hinders efficient charge separation, thereby limiting the photocurrent density and overall PEC performance (Chougale 2025; Folawewo & Bala 2022; Ong et al. 2018; Wahyuono et al. 2016). Consequently, addressing these limitations is essential for enhancing the light absorption capability, charge transfer efficiency, stability, and PEC performance of ZnO as a photoanodes. To overcome these challenges, various strategies have been developed to improve the PEC performance of ZnO photoanode.

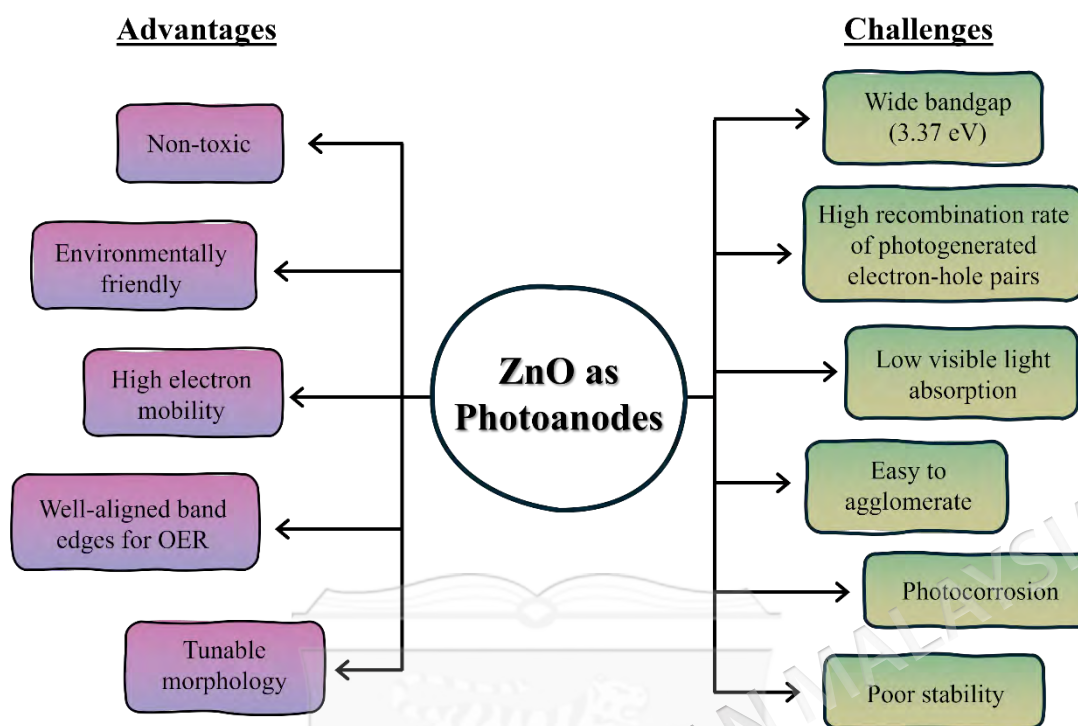


Figure 2.7 Properties and challenges of ZnO as photoanode.

2.4.2 Strategies to improve ZnO photoanodes

Despite the promising properties of ZnO for solar energy harvesting, its practical application is often hindered by its wide E_g and high charge carrier recombination rates. To overcome these limitations, various strategies have been developed to enhance the optical, electronic, and interfacial properties of ZnO photoanodes. These approaches aim to improve light absorption, promote efficient charge separation and transport, and suppress recombination losses. Common strategies include nanostructure engineering, heterostructure formation, surface modification, doping, and the incorporation of co-catalysts or conductive substrates. These strategies collectively enable ZnO photoanodes to achieve improved PEC performance and stability, advancing their potential for efficient solar-driven water splitting (Abdullah et al. 2023; Abdullah et al. 2025; Ong et al. 2018; Qiu et al. 2019). The strategies to improve performance of ZnO as illustrated in Figure 2.8.

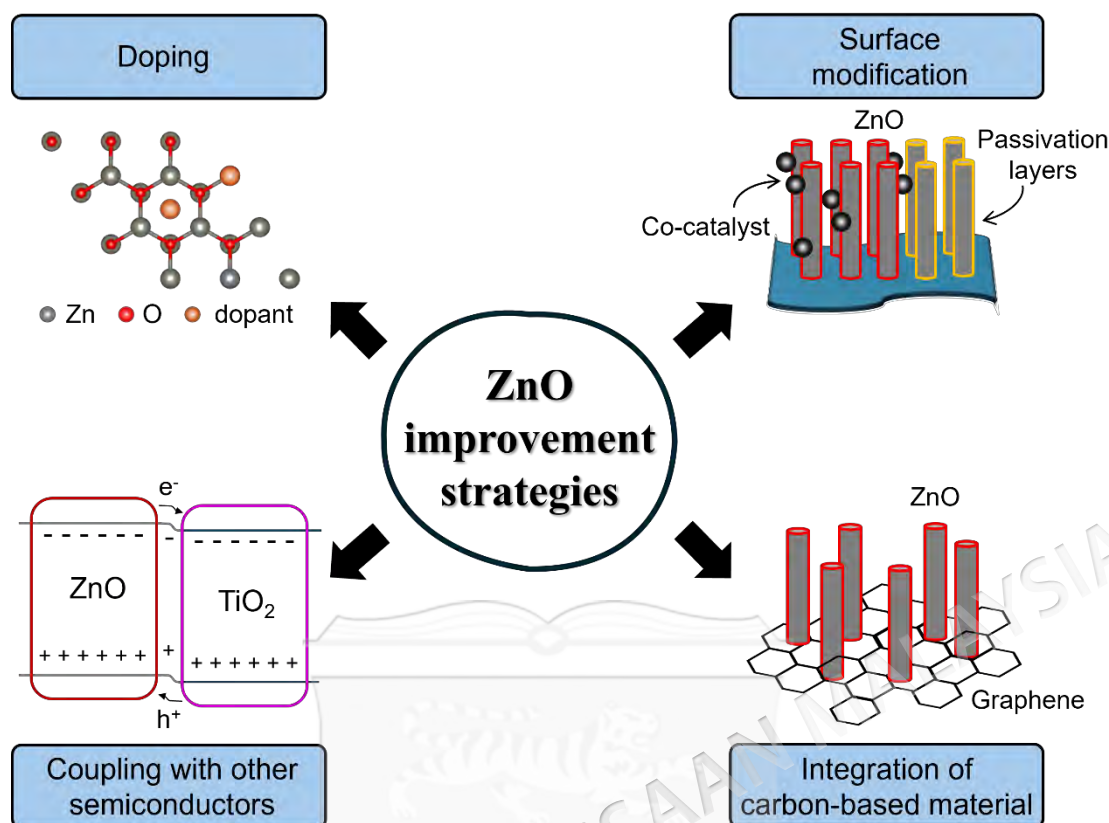


Figure 2.8 Strategies to improve performance of ZnO as photoanode.

a. Doping

Doping is a widely used approach to modify the physical and chemical properties of ZnO by introducing metal or non-metal impurities into its crystal lattice. This modification can effectively alter the E_g and shift the VB edge upward, thus enhancing charge separation and improving photocatalytic performance (Beura & Thangadurai 2018; Kang et al. 2019). Generally, ZnO behaves as an n-type semiconductor because of natural defects in its structure, such as oxygen vacancies (V_o), zinc interstitial (Zn_i), and zinc vacancies (V_{Zn}). These defects significantly affect its optical and electrical properties. The conductivity of ZnO can be enhanced at higher concentration of V_o , because these defects are believed to provide additional charge carriers (Pradeev raj et al. 2018).

As mentioned before, the PEC performance of a photoanode depends largely on its E_g and ability to absorb visible light. Through doping, a new intermediate energy levels can be introduced within the E_g , reducing the energy required for photon

excitation and extending light absorption into the visible region. Regardless of the dopant type, whether nitrogen, plasmonic Au, or iron (Fe), studies have shown an improvement in light absorption, efficient charge transfer, and higher photocurrent densities compared to undoped ZnO. For instance, N-doped ZnO nanorods produced a terraced band structure that produced a built-in electric field (Figure 2.9), facilitating more efficient separation of photogenerated $e^- - h^+$ pairs, exhibited a photocurrent of $\sim 0.16 \text{ mA/cm}^2$, compared to $\sim 0.08 \text{ mA/cm}^2$ for undoped ZnO at 1.10 V vs SCE in 0.50 M Na_2SO_4 electrolyte. Furthermore, stability measurements conducted at 0.80 V vs SCE showed that the current density of N-doped ZnO decreased slightly, which subsequently stabilized after 0.72 hours (Wang et al. 2015).

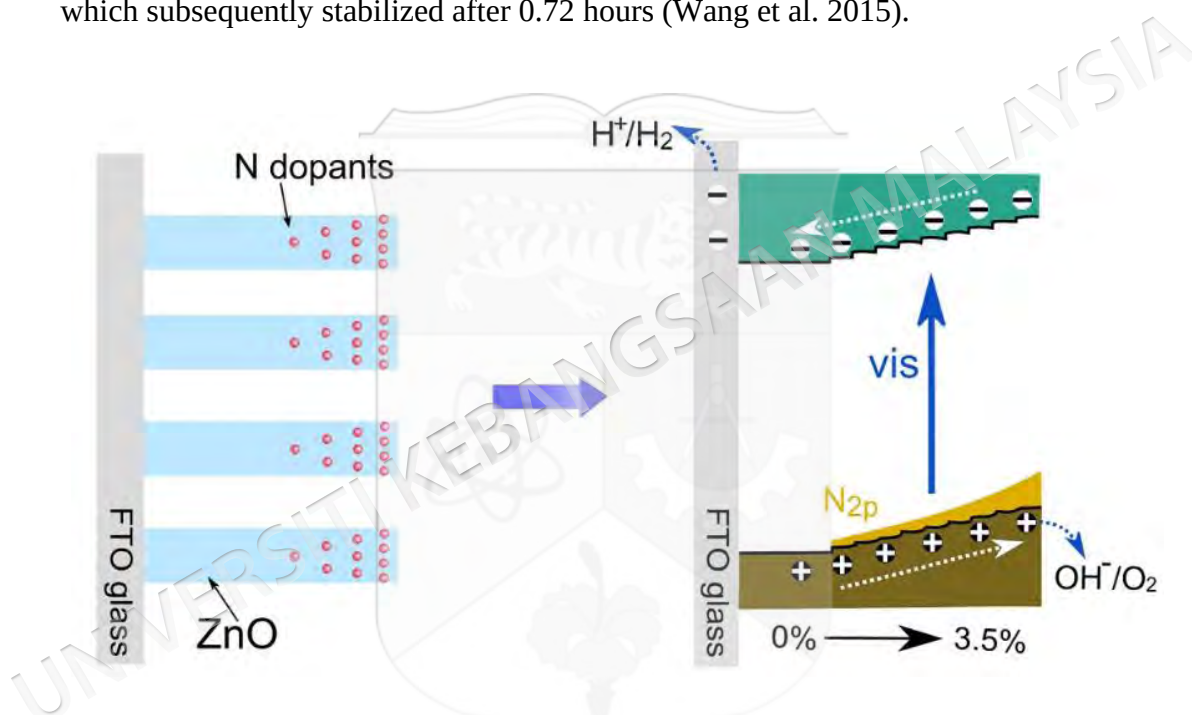


Figure 2.9 Schematic illustration of N-doped ZnO nanorods with a terraced band structure for enhanced charge carrier separation.

Source: Wang et al. (2015)

Meanwhile, Au-doped ZnO formed a well-defined interface between Au and ZnO nanorods. The existence of hot electron injection from plasmonic Au, has increased the photocurrent density from 0.0011 mA/cm^2 to $\sim 0.0036 \text{ mA/cm}^2$ at 1.10 V vs NHE under 0.015 mW/cm^2 light intensity in 0.50 M Na_2SO_4 electrolyte. Nevertheless, the Au-doped ZnO photoanode suffered from photocorrosion under continuous illumination at 1.20 V vs NHE, resulting in a 48% degradation in current density over a 3-hour period (Güler et al. 2023). Similarly, Fe-doped ZnO produced thinner and longer ZnO nanorods with a hexagonal wurtzite structure, leading to

improved light absorption efficiency. This morphology achieved a photocurrent density of 6 mA/cm^2 , generating 6.30 mmol of H_2 within 1 hour and achieving a STH efficiency of 4.70% using 1 M KOH of electrolyte (Rahmawati et al. 2024). These findings highlight the effectiveness of doping in enhancing the PEC performance of ZnO by improving light absorption, charge separation, and surface reactivity.

b. Surface modification

Although doping can improve the PEC performance of ZnO by introducing vacancies and modifying its electronic structure, achieving uniform dopant distribution remains a significant challenge. Also, when the dopant concentration becomes too high or unevenly distributed, it can generate deep trap states, where the defect levels located deep within the E_g are strongly capture the charge carrier. These trapped electron or hole tend to recombine rather than contribute to the reaction, resulting in low photocurrent and reducing PEC efficiency (Bünzli et al. 2014; Miao et al. 2019). Therefore, surface modification has emerged as another alternative to enhance the PEC performance of ZnO photoanodes.

By tailoring the surface properties through various techniques such as coating, etching, sensitization, or deposition of co-catalysts, researchers have been able to improve the surface reaction, charge transfer efficiency, and stability of ZnO while also reducing particle agglomeration. For instance, Cao et al. (2016) found that zinc ferrite/cadmium sulfide/ZnO (ZFO/CdS/ZnO) photoanode effectively suppressed photocorrosion and improved crystallinity. In this composite system, ZFO prevents the photocorrosion of CdS, while CdS helps to improve the visible light absorption of ZnO. Due to these synergistic effects, the rough surface of hexagonal structure of ZnO modified with ZFO/CdS exhibits 3.88 mA/cm^2 of current density at 0 V vs Ag/AgCl in $0.50 \text{ M Na}_2\text{S}$ electrolyte. Additionally, the ZFO/CdS/ZnO demonstrated robust stability by maintaining 85.1% of its original current density after 1 hour of illumination (Figure 2.10). However, it is important to note that CdS is a toxic material, which raises environmental concerns for large-scale application.

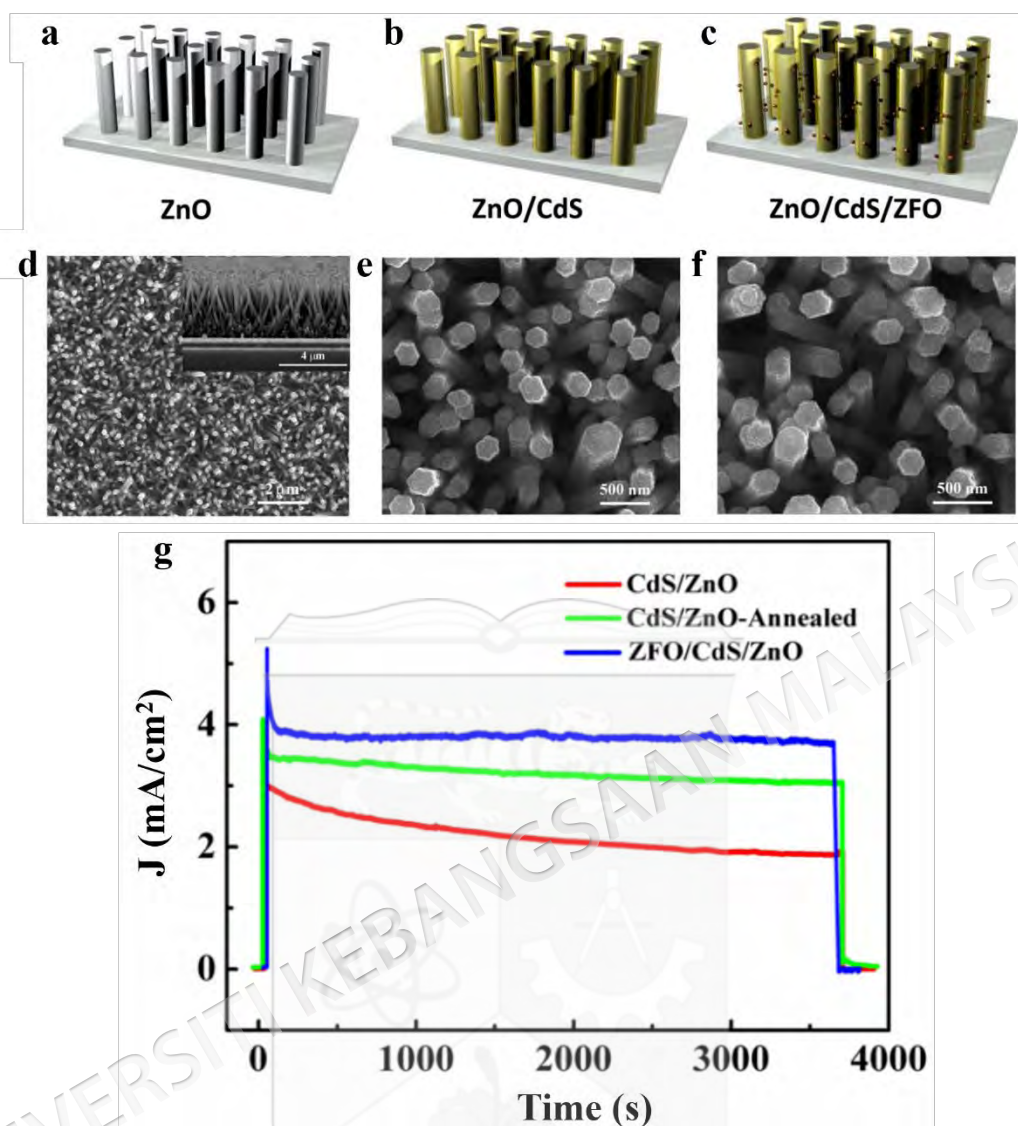


Figure 2.10 Schematic diagram of the synthesis process for (a) ZnO, (b) CdS/ZnO, (c) ZnO/CdS/ZFO. SEM images of (d) ZnO, (e) CdS/ZnO, (f) ZFO/CdS/ZnO. (g) Stability test results for CdS/ZnO, CdS/ZnO-Annealed and ZFO/CdS/ZnO.

Source: Cao et al. (2016)

To overcome the stability of the photoelectrode without toxic precursors, the introduction of passivation layers on the ZnO surface has proven effectively. Li et al. (2018) reported that coating ZnO nanorods grown on Ni-foam (NF) with a zeolitic imidazolate framework-8 (ZIF-8) layer successfully passivated surface states, reduce surface defects, and protected the underlying ZnO from photocorrosion (Figure 2.11). The subsequent deposition of nickel (II) hydroxide ($\text{Ni}(\text{OH})_2$) as a co-catalyst on the ZIF-8/ZnO/NF structure further enhanced interfacial charge transfer and reduced surface hole trapping. This modification achieving a stable photocurrent density of

1.95 mA/cm², which is significantly higher than bare ZnO/NF (0.92 mA/cm²) at 1.23 V vs RHE. Furthermore, the Ni(OH)₂/ZIF-8/ZnO/NF photoanode exhibited excellent stability, maintaining a nearly constant current density throughout a 3-hour stability test in 0.10 M KOH electrolyte (Li et al. 2018).

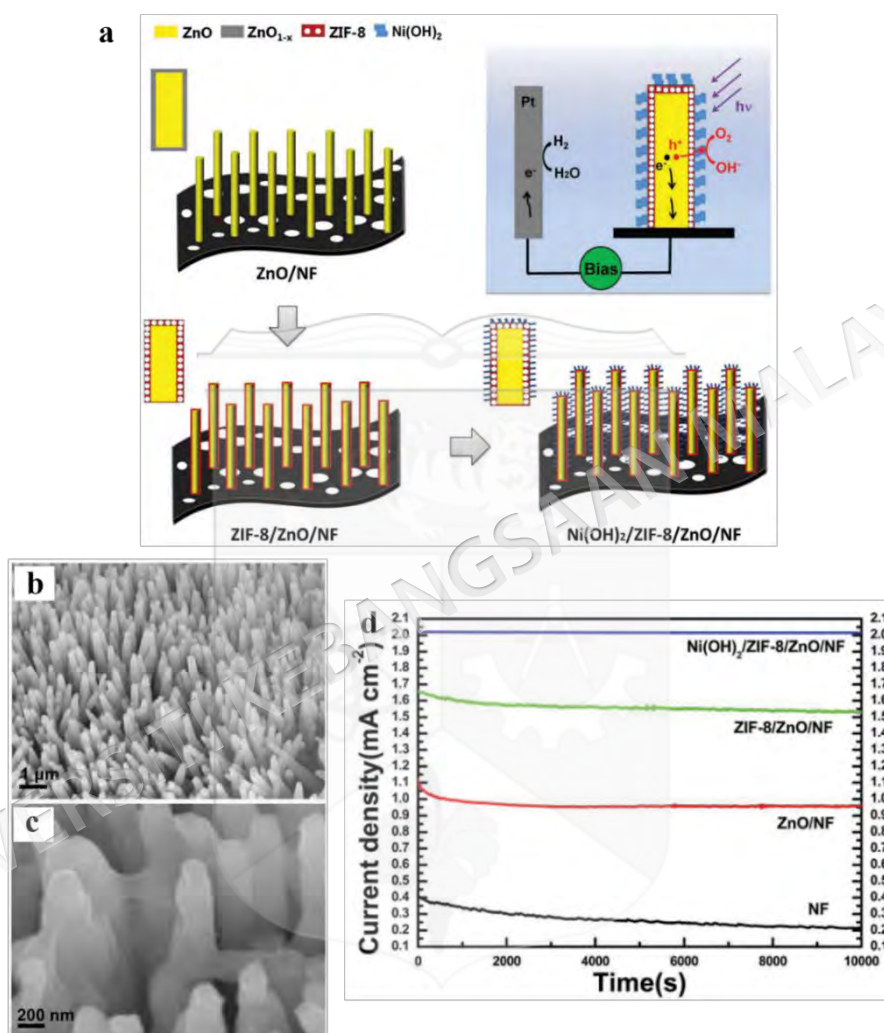


Figure 2.11 (a) Schematic illustration of the synthesis process of Ni(OH)₂/ZIF-8/ZnO/NF photoanode, including the proposed mechanism for PEC water splitting. (b, c) SEM images of Ni(OH)₂/ZIF-8/ZnO/NF photoanode at different magnifications. (d) Stability comparison of the NF, ZnO/NF, ZIF-8/ZnO/NF and Ni(OH)₂/ZIF-8/ZnO/NF photoanodes measured at 1.23 V vs RHE.

Source: Li et al. (2018)

In addition the surface modification, depositing plasmonic Au on ZnO surfaces has been widely studied to boost light absorption and charge transfer. Saboor et al. (2021) found that Au nanoparticles deposited on ZnO nanorods on FTO (ZNs-Au)

maintained the nanorod structure while enabling efficient hot electron injection from Au to ZnO. The plasmonic effect of Au not only extend light absorption into the visible range but also reduces the activation energy required for interfacial reactions. The highest performance was observed when Au was deposited for 60 seconds, yielding a photocurrent density of 0.66 mA/cm^2 at 1.00 V vs SCE in $0.50 \text{ M Na}_2\text{SO}_4$ electrolyte. Overall, these findings demonstrate that surface modification strategies, such as coating ZnO with other materials, decorating co-catalysts, and deposition with plasmonic materials, can successfully enhance light absorption, charge transfer, and PEC efficiency of ZnO-based photoanodes.

c. Coupling with other semiconductors

Coupling ZnO with other semiconductors has emerged as an effective strategy to overcome its intrinsic limitations in light absorption, charge recombination, and stability. Surface modification can protect the ZnO layer from chemical corrosion and photocorrosion, however, it may also hinder electron transfer when the protecting coating is too thick or poorly aligned, thereby increasing surface resistance and reducing PEC performance (Chougale 2025). To address these challenges more efficiently, heterojunction engineering offers a complementary approach by coupling ZnO with other semiconductors that having different E_g and appropriate band alignments to straddle the redox potential of H_2O . Such heterojunctions enhance charge separation and broaden the light absorption range, thus improving the PEC performance (Opoku et al. 2017).

Usually, ZnO is coupled with a narrow E_g semiconductor like gallium oxynitride (GaON) or zinc cobalt oxide (ZnCo_2O_4). For example, Khan et al. (2018) demonstrated that the formation of GaON/ZnO nanoflowers effectively reduced the E_g of ZnO to 2.58 eV , resulting in a photocurrent density of 1.20 mA/cm^2 at 1.23 V vs SCE $0.50 \text{ M Na}_2\text{SO}_4$ electrolyte. Besides, the stability test indicated that the current density dropped about 0.01 mA/cm^2 after tested for 0.30 hours at 1.23 V vs SCE. A similar enhancement was reported by Maity et al. (2021), where the construction of an n-p heterojunction between n-ZnO and p- ZnCo_2O_4 achieved uniform deposition of ZnCo_2O_4 shells by adjusting the electrodeposition time (Figure 2.12 (a – h)). The results

show that 3 minutes deposition yielded the optimized thickness, which broadened the light absorption range and provided favourable band alignment for electron transfer during the OER. In contrast, 4 minutes deposition resulted in excessively thick ZnCo_2O_4 layer. With a suitable shell thickness, the p- ZnCo_2O_4 /n-ZnO photoanode achieved a photocurrent density of 1.58 mA/cm^2 at 1.23 V vs RHE in $0.50 \text{ M Na}_2\text{SO}_4$, along with a lower onset potential compared to ZnO. Furthermore, p- ZnCo_2O_4 /n-ZnO demonstrated stable PEC performance, produced 0.02 mmol/cm^2 of H_2 gas after 2 hours (Figure 2.12 (i)). The energy band diagram in Figure 2.12 (j) reveals that the VB and CB of the ZnCo_2O_4 remain at higher energy levels than those of ZnO even after contact and subsequently E_f alignment, successfully forming a type-II p-n heterojunction. Therefore, photogenerated electrons transfer is from the CB of p- ZnCo_2O_4 to the CB of n-ZnO to facilitate H_2 production, while the photogenerated holes rapidly move from the VB of n-ZnO to the VB of p- ZnCo_2O_4 to produce O_2 .

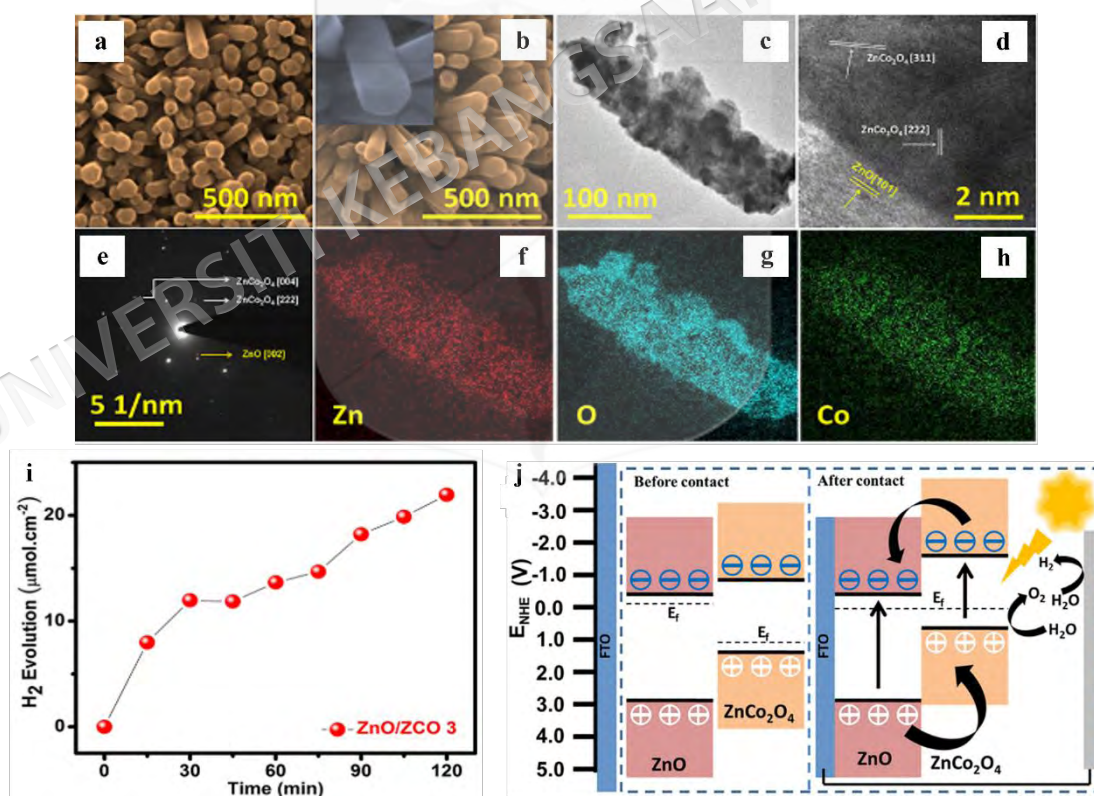


Figure 2.12 Morphological and structural characterization: FESEM images of (a) ZnO and (b) p- ZnCo_2O_4 /n-ZnO, (c) TEM, (d) HRTEM, and (e) SAED pattern of the heterojunction, and (f - h) elemental mapping of Zn, O, and Co. (i) Photocatalytic H_2 production of the optimized photoanode. (j) Proposed band energy diagrams of n-ZnO and p- ZnCo_2O_4 before and after contact.

Source: Maity et al. (2021)

In addition, coupling ZnO with semiconductors of comparable E_g , such as TiO₂ has also shown promising results. Gasparotto et al. (2019) demonstrated that controlling the TiO₂ content and thickness during sputtering resulted in intimate interfacial contact. This modification maintained a E_g of ~ 3.25 eV and improved charge transfer, yielding a photocurrent density of 0.93 mA/cm^2 at 0.25 V vs Ag/AgCl in 0.10 M NaOH electrolyte. In summary, these studies show that combining ZnO with other semiconductors, has proven to be a reliable method to overcome the limitations of ZnO and enhancing the PEC performance.

d. Integration of carbon-based materials

Besides E_g alignment, the lattice mismatch between ZnO and other materials is also an important factor to ensure strong interfacial contact, which directly affects stability and PEC performance (Geng et al. 2013). To overcome these challenges, integrating ZnO with carbon-based materials has emerged as one of the promising strategies. Unlike many metal oxides, carbon-based materials have flexible structures that naturally can fit onto the ZnO surface, promoting better interfacial contact and charge transfer (Saeed et al. 2020). Carbon-based materials, such as carbon nanotubes (CNTs), reduced graphene oxide (rGO), graphene oxide (GO), graphitic carbon nitride (g-C₃N₄) or graphene offer excellent electrical conductivity, high surface area, and strong chemical stability (Ong et al. 2018; Pratomo et al. 2023; Raizada et al. 2019). These properties facilitate faster charge transfer, suppress $e^- - h^+$ recombination, and significantly enhance the PEC efficiency of ZnO photoanodes.

Carbon-based materials can act not only as an electron acceptor but also as efficient charge transfer mediator. In ZnO/rGO systems, graphene sheets act as conductive pathways and electron acceptors, extending the absorption wavelength and reducing the E_g energy to facilitates electron transfer (Darvishi et al. 2017; Wang et al. 2020). As shown in Figure 2.13 (a, b), rGO nanosheets act as conductive bridges connecting the dispersed ZnO microspheres. This will promote the efficient separation of photogenerated carriers. Consequently, the mass ratio of rGO at 1% (ZrG-1) reduced charge transfer resistance (R_{ct}) and enhanced H₂ production to 0.65 mmol/h/g in $0.25 \text{ M Na}_2\text{SO}_3$ - $0.35 \text{ M Na}_2\text{S}$ (Figure 2.13 (c ,d)) (Wang et al. 2020). In contrast,

Mahala et al. (2020a) incorporated carbon dots onto 2D sheets using a dip-coating method to form ZnO/carbon dots (ZnO/C) structure. The resulting uniformly distributed carbon dots act as efficient light absorbers and charge mediators (Figure 2.13 (f)). The ZnO/C prepared with a 15-minute dip-coating time exhibited an improvement in PEC properties, achieving a photocurrent density of 2.05 mA/cm² at 0.60 V vs Ag/AgCl. Furthermore, the onset potential shifted from -0.40 V for ZnO to -0.70 V for ZnO/C dots under 100 mW/cm² illumination in 0.5 M Na₂SO₄. Although the ZnO/C displayed a slight performance decay over a 2-hour continuous stability test, the current density decreased by only 0.18 mA/cm² (Figure 2.13 (g)).

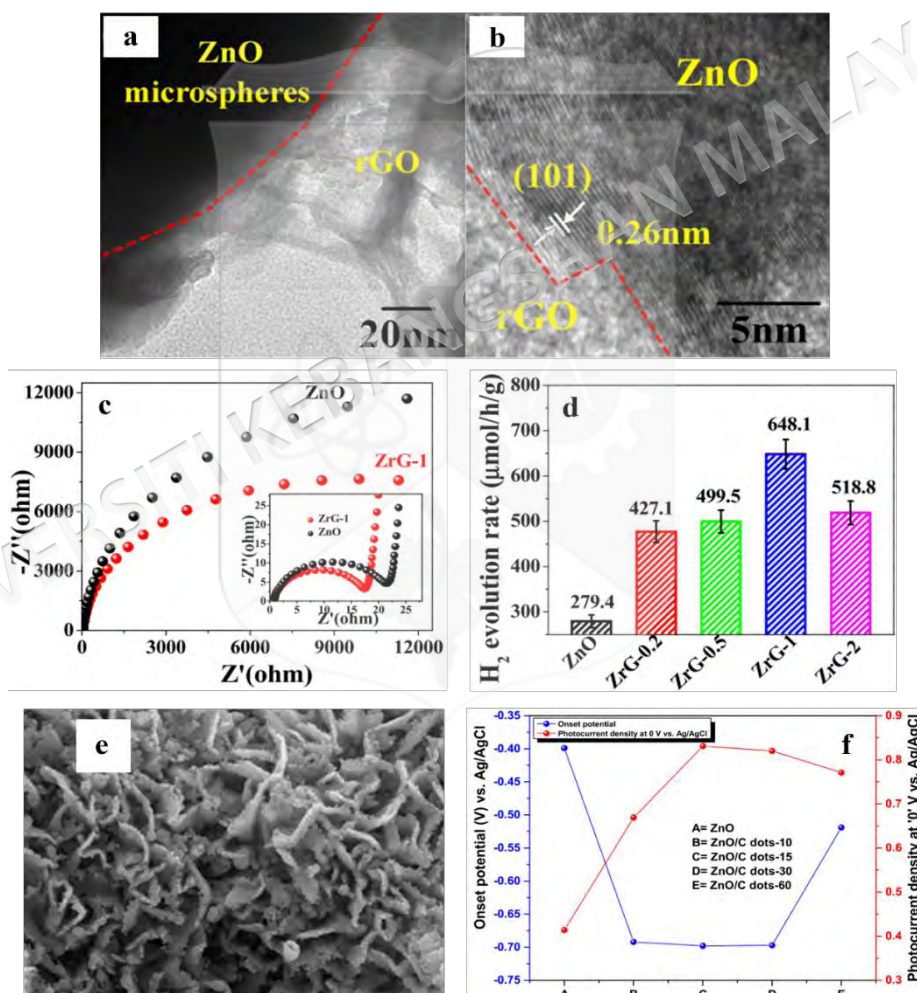


Figure 2.13 (a, b) HRTEM images of ZnO/rGO. (c) EIS plots at low and high frequencies (inset) of ZnO and ZrG-1. (d) H₂ production rates. (f) FESEM images of ZnO/C dots-15. (g) Comparison of onset potentials and photocurrent density.

Source: Wang et al. (2020) and Mahala et al. (2020a)

Similarly, coupling ZnO with g-C₃N₄ (ZnO/C₃N₄) results in the formation of a porous ZnO/C₃N₄ heterojunction with a large surface area that improves interfacial charge transport and exhibit higher photocurrent density of 0.95 mA/cm², compared to 0.41 mA/cm² for ZnO at 0.60 V vs RHE under 100 mW/cm² using 0.50 M Na₂SO₄ electrolyte. In addition, ZnO/C₃N₄ shows a cathodic onset potential shift of 0.06 V compared to 0.20 V for ZnO, indicating improved photoresponse and faster interfacial charge transfer. Besides, stability tests revealed that the ZnO/C₃N₄ showed a slight initial performance drop but remained stable for up to 1 hour of continuous testing (Mahala et al. 2020b). Recently, Siahshahlan et al. (2025) investigated the effects of graphene concentrations on ZnO. The result showed that graphene promoted better conglomeration of ZnO grains while forming a conductive intergranular layer. This ZnO/Graphene reduces the E_g and improve PEC performance (1.10 mA/cm² at 0.50 V vs SCE in 1 M KOH electrolyte). However, while increasing graphene concentrations improves performance but the excessive amounts may hinder charge transfer and reduce the overall efficiency (Salem et al. 2018).

Overall, these findings demonstrate that the PEC performance of ZnO can be improved through various modification strategies, as summarized in Table 2.1. Among these approaches, the incorporating of carbon-based materials into ZnO photoanodes has emerged as one of the effective methods for overcoming the intrinsic limitations of ZnO. Carbon-based materials not only enhance charge transfer and suppress charge recombination but also significantly improves PEC performance while reducing the onset potential for OER. These improvements highlight the role of carbon-based materials in improving the efficiency of ZnO-based photoanodes. Among the available carbon-based materials, graphene stands out due to its exceptional electrical conductivity and highly delocalized π -electron network, which offer advantages compared to rGO, carbon-dots, or g-C₃N₄. However, despite these promising properties, studies on ZnO coupled with graphene specifically for photoanode remain limited. This research gap highlights the need for further exploration of graphene-based support to fully assess the potential contribution of graphene in PEC systems.

Table 2.1 Summary of recent modification strategies and their PEC performance for H₂ production.

Material	Strategy	Electrolyte	Photocurrent density (mA/cm ²)	Stability	H ₂ production	Reference
N-doped ZnO	Doping	0.5 M Na ₂ SO ₄	~0.16 at 1.10 V vs SCE	The current density slightly decreased and stabilized after 0.72 hours	-	(Wang et al. 2015)
Au-doped ZnO		0.5 M Na ₂ SO ₄	~0.0036 at 1.10 V vs NHE	Suffered from photocorrosion, resulting in a 48% degradation in current density over a 3-hour	-	(Güler et al. 2023)
Fe-doped ZnO		1 M KOH	6	-	3.60 mmol/hour	(Rahmawati et al. 2024)
ZFO/CdS/ZnO	Surface modification	0.5 M Na ₂ S	3.88 at 0 V vs Ag/AgCl	Maintained 85.1% of its original current density after 1 hour	-	(Cao et al. 2016)
ZIF-8/ZnO/Ni-foam		0.1 M KOH	1.95 at 1.23 v vs RHE	Excellent stability, maintaining a nearly constant current density throughout a 3-hour	-	(Li et al. 2018)
ZnO/Au/FTO		0.5 M Na ₂ SO ₄	0.66 at 1.00 V vs SCE	-	-	(Saboor et al. 2021)
GaON/ZnO	Coupling with other semiconductor	0.5 M Na ₂ SO ₄	1.20 at 1.23 v vs SCE	Current density dropped about 0.01 mA/cm ² after tested for 0.30 hours	-	(Khan et al. 2018)
p-ZnCo ₂ O ₄ /n-ZnO		0.5 M Na ₂ SO ₄	1.58 at 1.23 V vs RHE	-	0.02 mmol/cm ² /2 hours	(Maity et al. 2021)
ZnO/TiO ₂		0.1 M NaOH	0.93 at 0.25 V vs Ag/AgCl	-	-	(Gasparotto et al. 2019)

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ZnO/rGO		0.25 M Na ₂ SO ₃ / 0.35 M Na ₂ S	-	-	0.65 mmol/g/hour	(Wang et al. 2020)
ZnO/carbon dots	Integration of carbon-based materials	0.5 M Na ₂ SO ₄	2.05 at 0.60 V vs Ag/AgCl	Performance decay over a 2-hour, the current density decreased by only 0.18 mA/cm ²	-	(Mahala et al. 2020a)
ZnO/g-C ₃ N ₄		0.5 M Na ₂ SO ₄	0.95 at 0.60 V vs RHE	Initial performance slightly drops but remained stable for up to 1 hour	-	(Mahala et al. 2020b)
ZnO/graphene		1 M KOH	1.10 at 0.50 V vs SCE	-	-	(Siahsahlan et al. 2025)

2.5 GRAPHENE-BASED SUPPORT

Graphene-based materials have gained significant attention as efficient supporting material in PEC water splitting due to their zero-band gap behaviour, outstanding electrical conductivity, large specific surface area, high electron mobility and excellent chemical and thermal stability. Graphene, discovered by Novoselov and Geim (2004), consists of a single atomic layer of sp^2 bonded carbon atoms arranged in a 2D honeycomb lattice. With a theoretical specific surface area of $\sim 2600 \text{ m}^2/\text{g}$, graphene provides more adsorption and active sites that support interfacial reactions. Also, the 2D structure of graphene allows semiconductor nanostructures to disperse uniformly on graphene surface, forming a larger contact interface between semiconductors and graphene (Cao & Yu 2016; Jilani et al. 2020; Saeed et al. 2020). In addition, the extended π -electron structure in graphene enables rapid charge transfer, promoting efficient electron transfer during photocatalytic H_2 reaction. Because of these remarkable properties, graphene-based are recognized as highly promising support for improving PEC performance.

2.5.1 Synthesis method of graphene

Graphene synthesis strategies are generally categorized into top-down (exfoliation of GO, micromechanical cleavage) and bottom-up (CVD) approaches (Bhuyan et al. 2016; Hu et al. 2017; Plutnar et al. 2018). The pioneering discovery of graphene was achieved through micromechanical cleavage of highly ordered pyrolytic graphite. While this method produces high-quality single layer graphene (SLG), it is thermodynamically unstable in a free-standing state and suffers from poor reproducibility and a lack of substrate control (Bhuyan et al. 2016; Plutnar et al. 2018). To address scalability, chemical exfoliation has been explored. For instance, Szirmai et al. (2019) demonstrated that saturating potassium-doped graphite can formed few-layer graphene. However, this method often results in small flake sizes and structural defects.

CVD methods were frequently used for synthesizing large-area, high-quality monolayers of graphene on various metal substrates. The growth mechanism is determined by the carbon solubility of the substrate. As for copper (Cu) substrates, Cu exhibits low carbon solubility, leading to monolayer graphene formation. Rosman et al.

(2021) reported that the CH_4 flow rate is a critical parameter on Cu, where high concentrations of CH_4 flow rates lead to higher decomposition rates and increased layer thickness. As for Ni substrate, Ni has a high carbon solubility (Lahiri et al. 2011). At high temperatures, carbon atoms diffuse into the bulk Ni, and upon cooling, it precipitate to the surface to form graphene and this process known as segregation mechanism (Chen et al. 2015). While this allows for stronger chemical bonding between carbon and Ni, precise control over the number of graphene layers remains a challenge.

In addition, electrodeposition SLG on stainless steel substrate has shown promising approach. However, a significant limitation of most 2D graphene synthesis on flat substrates like Cu or Ni foils, is the transfer process (Jeong et al. 2022; Rosman et al. 2021). This is because when moving graphene from the growth substrate to the final substrate often introduces mechanical damage where graphene layer easily tearing or wrinkling. Also, it can introduce chemical defects and increase interfacial resistance which can introduce poor physical contact between the transferred graphene and the target substrate. This disadvantage highlights the importance of direct growth methods, such as the CVD synthesis of graphene directly onto 3D substrates. The 3D graphene has gained increasing attention due to its unique architecture and superior properties compared to conventional 2D graphene sheets (Table 2.2).

Table 2.2 Comparison of the structural and electrochemical properties of 2D and 3D graphene.

Properties	2D graphene	3D graphene
Surface area	Acceptable	Good
Mechanical strength	Acceptable	Good
Electrical conductivity	Good	Good
Resistance	Acceptable	Good
Restacking tendency	Yes	Acceptable
Mass transport	Acceptable	Good

It is called 3D graphene because the graphene is grown on a 3D template. One of the advantages of 3D graphene is the ability to prevent the restacking of graphene layers, preserving the intrinsic properties of individual sheets, such as high electrical conductivity and rapid ion transfer (Mohd Shah et al. 2021; Nine et al. 2017). The

interconnected porous network of 3D graphene provides a significantly higher surface area, more active sites, and efficient electron transport pathways. Depending on the synthesis method, 3D graphene can be produced in various forms, including foams, aerogels, and hydrogels, which all of it offer high porosity, enhanced light absorption, excellent mechanical and electrical stability, improves electrolyte pathway, and enhanced accessibility to catalytic sites (Kuang et al. 2020).

The 3D graphene can be synthesized using top-down or bottom-up methods (Agrawal 2025). For top-down methods, bulk carbon materials are physically or chemically exfoliated or reconstructed into nanoscale 3D architectures, making these methods simple and highly scalable. For example, 3D N-doped graphene aerogel synthesized using thermal treatment of GO and nitrogen sourced from g-C₃N₄ produced ultrathin transparent graphene nanosheets with irregular carbon, oxygen, and nitrogen arrangements (Maouche et al. 2020). These structures achieved a H₂ production rate of 0.040 mmol/g over 3 hours, attributed to enhanced charge separation induced by nitrogen doping and the increased availability of active sites due to the porous architecture.

Besides that, hydrothermal method is commonly used to produce porous 3D graphene due to its simplicity and ability to control morphology through solution-based reactions influenced by vapor pressure and reaction conditions (Figure 2.14) (Miao et al. 2018). For instance, 3D N-doped graphene aerogel decorated with Pt nanoparticles were synthesized from GO and poly(oxypropylene)diamine D400 precursors. The GO concentration and pH strongly influenced the resulting morphology, where Pt exhibit interconnected branch adhered to an N-doped graphene aerogel surface (Zhou et al. 2018). Besides that, 3D graphene has been prepared using various diamine crosslinkers, such as benzidine, 2,2'-dimethyl-4,40-biphenyldiamine (DMPDA), and 4,40-diaminodiphenylmethane (MDA). The GO-benzidine displayed a rough and highly porous surface that facilitated efficient excitation of GO vacancies under irradiation. Interestingly, despite having a lower specific surface area, GO-benzidine achieved a higher H₂ production rate of around 0.69 mmol/g/h (Zhou et al. 2020), demonstrating that PEC performance is not fully depends by surface area.

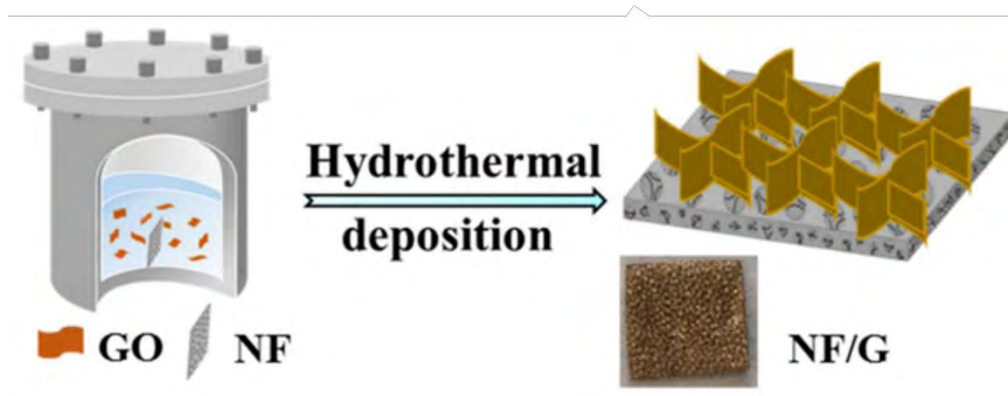


Figure 2.14 Schematic representation of the hydrothermal growth process for 3D graphene.

Source: Miao et al. (2018)

In contrast, bottom-up methods construct 3D graphene structures directly from molecular precursors. Among these, CVD is one of the most widely used and effective techniques for producing high-quality graphene at large scales (Figure 2.15). Typically, CVD grown graphene exhibits superior electrical conductivity compared to graphene derived from GO reduction. In CVD processes, metal substrates such as Cu, Ni, Fe, and cobalt (Co), act as templates, substrates, or catalysts that decompose hydrocarbon gases and facilitate the formation of sp^2 hybridized carbon networks (Banciu et al. 2020; Tynan et al. 2016; Wang et al. 2016). Cu and Ni are favored due to their lattice matching with graphene, like Cu (111) and Ni (111) surfaces have lattice constants of $\sim 2.56 \text{ \AA}$ and $\sim 2.49 \text{ \AA}$, respectively, closely matching the lattice constant of graphene of $\sim 2.46 \text{ \AA}$. Despite these advantages, precise control over the number of graphene layers and the subsequent etching of 3D metal templates remain significant challenges in CVD.

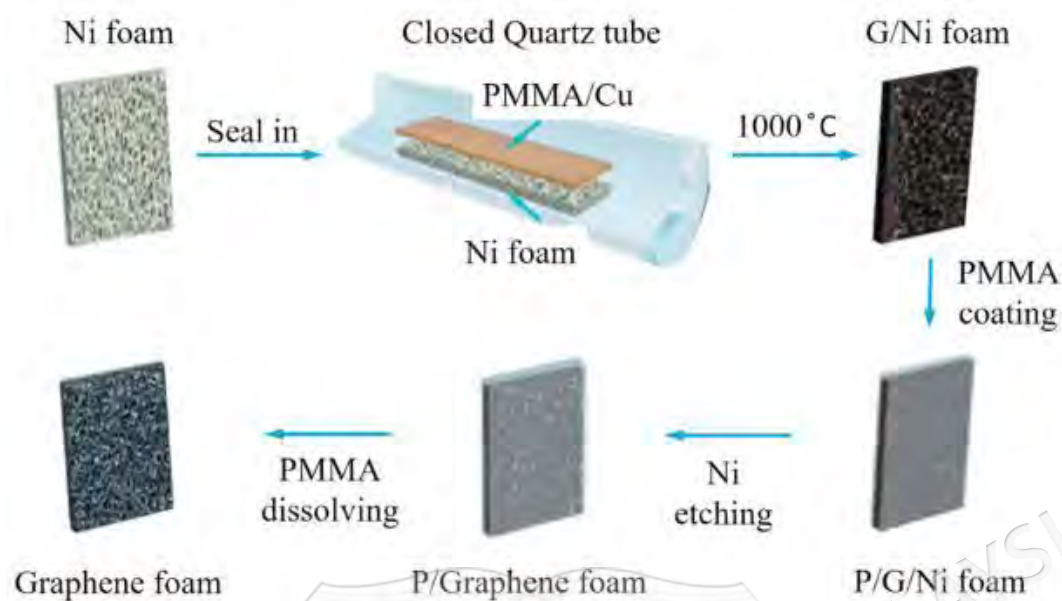


Figure 2.15 Schematic illustration of the CVD growth process for 3D graphene.

Source: Wang et al. (2016)

The catalytic activity and carbon solubility of the metal substrates strongly influence the CVD growth mechanism, and it affects the number of graphene layers. Hydrocarbon decomposition on metal surfaces provides active carbon species, lowering the activation energy required for carbon incorporation (Mohd Shah et al. 2021). Early developments in 3D graphene involved growing graphene directly on metal foams such as Ni, Cu, Fe, and Co, followed by etching the templates using HCl (Tynan et al. 2016). After etching, the porosity of the foam was maintained, and clear grain boundaries were observed. Furthermore, graphene grown on Ni, Fe, and Co-foam exhibited higher crystallinity, whereas graphene grown on Cu-foam showed more structural defects, as confirmed by defect peak in Raman spectra in Figure 2.16. Also, the graphene layers can be up to three and more layers, depending on the foam template used.

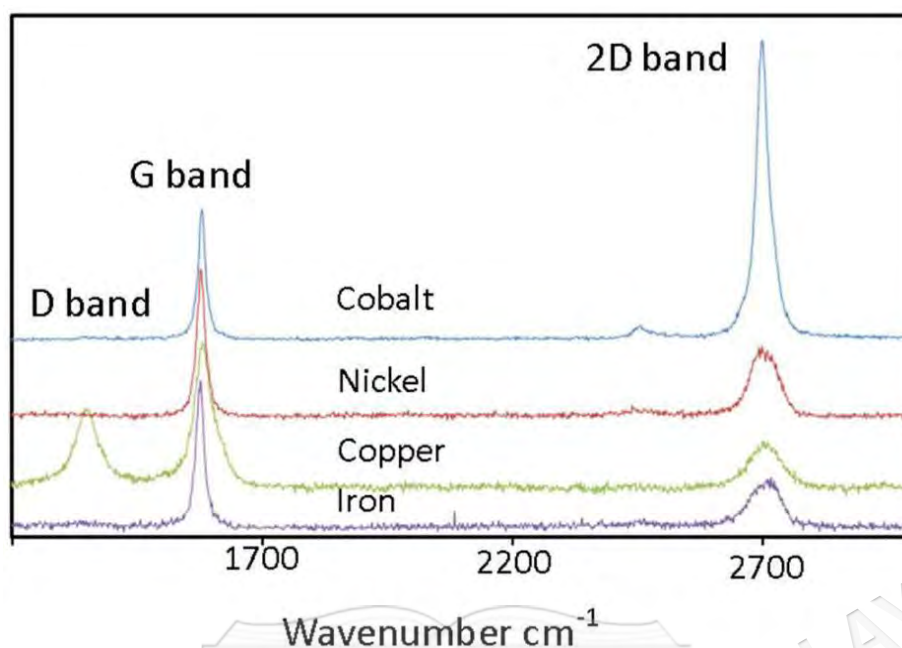


Figure 2.16 Raman spectra of graphene grown on various metals substrates.

Source: Tynan et al. (2016)

Subsequent advancements focused on maintain the metal foam without etching. Bello et al. (2013) reported high-quality graphene uniformly coating Ni-foam, with wrinkles and ripples attributed to differences in thermal expansion between graphene and Ni during CVD reaction. Similar observations were made by Mohd Shah et al. (2022), where increasing annealing time improved graphene coverage on Ni-foam and reduced surface roughness of the Ni-foam, likely due to optimized growth kinetics. This graphene-Ni interface is expected to enhance corrosion resistance, and advantage for PEC applications.

Further studies demonstrated the successful growth of 3D graphene on both Cu and Ni-foams using CH_4 as the carbon source (Drieschner et al. 2016). The results indicated that graphene more readily and uniformly coated Ni-foam compared to Cu-foam, even at short growth times (around 5 minutes), without noticeable defects. This difference can be attributed to Ni lattice constant and higher carbon solubility compare to Cu (Muñoz & Gómez-Aleixandre 2013). To achieved uniform graphene deposition on Cu substrates, CH_4 concentration required careful control (Sirat et al. 2017). Also, the number of graphene layers increased with longer growth durations, demonstrating the precise tunability of CVD process.

With proper adjustment, the CVD method can produce mechanically stable graphene on 3D porous substrates that retain their structure even after the metal template is removed. Nevertheless, the final graphene quality is strongly influenced by the etching step, which must be carefully controlled to prevent defect formation or damaging the 3D framework. In addition, the resulting 3D graphene may also become hydrophobic after etching, which can affect its performance in aqueous environments. Recent findings further indicate that leaving the metal foam unetched can produce graphene with excellent surface coverage, strong interfacial adhesion, and enhanced electrochemical stability. These findings suggest that the choice whether to retain or remove the metal substrate should be based on the intended application and required structural characteristics.

2.5.2 Substrate candidates for graphene

When growing graphene on conductive metal substrates, two main factors must be considered: (i) the lattice mismatch, and (ii) the interaction between the metal and the graphene (Dahal & Batzill 2014). As discussed in Section 2.5.1, Ni is unique from other metals because its lattice constant closely matches that of graphene. Consequently, Ni-based substrates such as Ni-foil and Ni-foam are commonly employed as conductive supports in PEC water splitting (Deokar et al. 2020; Mohd Shah et al. 2022; Qu et al. 2016; Rosman et al. 2023; Rybin et al. 2018; Yu et al. 2024). These materials are selected not only for their lattice compatibility but also for their excellent electrical conductivity, mechanical robustness, and corrosion resistance in alkaline media. While Ni-foil and Ni-foam share similar advantages, their morphological differences determine their specific role in PEC applications.

Ni-foil as a standard 2D planar reference, offering a well-defined geometric area suitable for fundamental studies. However, its flat surface provides limited active sites and relies on specular light reflection (Pehlivan et al. 2019; Qu et al. 2016; Rybin et al. 2018). In contrast, Ni-foam represents the most advanced 3D substrate. Its interconnected porous structure not only maximizes the specific surface area but also significantly enhances the PEC performance by promoting multiple internal light scattering and enabling efficient electrolyte pathway (Lee et al. 2017; Mohd Shah et al.

2022; Pehlivan et al. 2019). Despite these morphological differences, the high conductivity and favourable surface chemistry of these Ni-based substrates facilitate rapid charge transfer between the photoactive layer and the external circuit, thereby improving PEC efficiency and electrode stability during prolonged operation.

2.6 EFFECT OF ZnO/GRAPHENE/NICKEL ON PEC PERFORMANCE

Coupling graphene with ZnO photoanodes has proven to be an effective strategy for overcoming the inherent limitations of ZnO, especially its fast charge recombination and stability over photocorrosion (Ong et al. 2018; Raizada et al. 2019). To further enhance performance, ZnO/graphene composites are frequently grown on Ni-based substrates using methods such as CVD or hydrothermal, as these substrates provide high electrical conductivity and have a strong interfacial interaction that increases accessible surface area and facilitates charge transfer (Chen et al. 2018; Pratomo et al. 2023). In this structure, graphene can act as a highly efficient electron transfer and electron mediator, thereby reducing recombination losses. As a result, the ZnO/graphene/Ni configuration significantly improved photocurrent density, enhanced charge separation efficiency, and improved long-term stability during PEC water splitting for H₂ production.

2.6.1 Synthesis methods for photoanode material

The synthesis of ZnO/graphene/Ni photoelectrodes involves the layering of three main components: ZnO as the photoactive semiconductor, graphene as the support or electron mediator, and Ni-based material as the conductive metal substrate (Gadisa et al. 2021; Mohd Shah et al. 2022). The process starts with the Ni substrates such as foil or foam, which offer excellent electrical conductivity and serves as a robust template for graphene growth. Subsequently, the graphene layer uses its exceptional conductivity to facilitate rapid charge transfer from the ZnO, effectively suppressing the recombination of photogenerated $e^- - h^+$ pairs. In the final step, ZnO nanostructures are grown on directly onto the graphene coated Ni substrate to form the photoelectrode. Importantly, the quality of the interfaces between ZnO, graphene, and Ni determines the PEC performance, as it directly influences the electron mobility, light absorption efficiency,

and the long-term stability of the photoelectrode for PEC applications (Dahal & Batzill 2014).

Various techniques are used to synthesis these materials, either through a single-step or multi-step process, with each methods offering different levels of control over morphology, crystallinity, and surface coverage (Plutnar et al. 2018). These techniques can be categorized into physical and chemical methods (Figure 2.17). Physical methods usually depend on the external energy sources such as heat, plasma, or mechanical stress, where it can physically breakdown or deposit materials (Toufani et al. 2020; Zhang et al. 2021). These methods often ensure strong interfacial bonding and uniform dispersion of ZnO, facilitating efficient charge transfer between ZnO and graphene. In contrast, chemical methods involve the reaction of the precursors through chemical reactions to build the material atom-by-atom or molecule-by-molecule, either in solution or gas phase (Basnet & Chatterjee 2020). These methods allow for the controlled coating of ZnO nanoparticles onto the graphene/Ni surface, enabling precise tuning of morphology, loading content, and surface coverage. Nevertheless, each approach influences the structural, optical, and electronic properties of the ZnO/graphene/Ni, thereby significantly affecting the PEC performance. Further discussion on the synthesis methods will be presented in the next section.

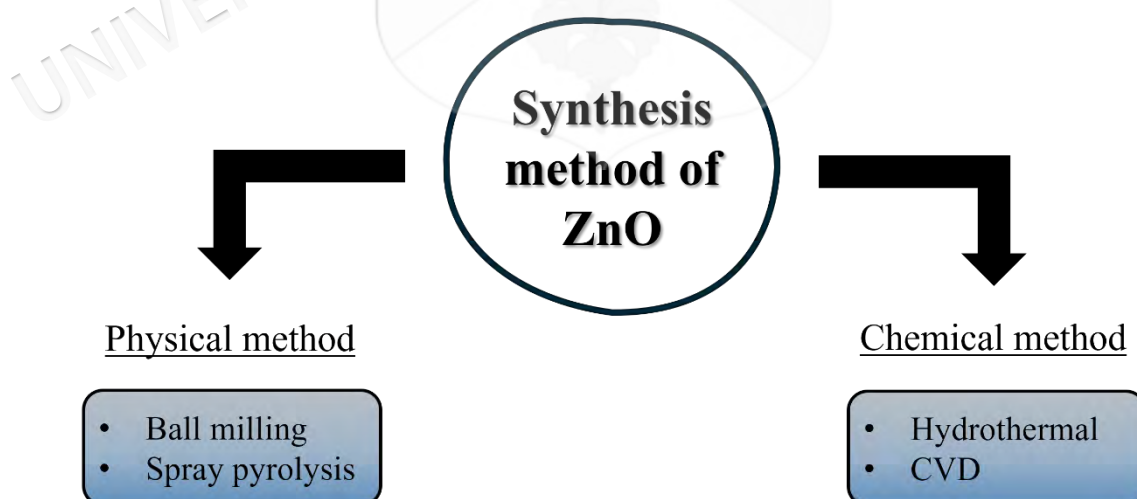


Figure 2.17 Overview of the various synthesis methods for ZnO/graphene/Ni.

a. Physical methods

Ball milling is an attractive approach for synthesizing ZnO/graphene due to its scalability and environmentally friendly. This method relies on mechanical collisions to force ZnO and graphene into close contact, forming strong interfacial bonds. Yin et al. (2019) demonstrated that ZnO/graphene prepared by this method enhances light absorption by external planar anisotropy and flake-like morphology of graphene after ball milled. Additionally, adjusting the milling duration can effectively control the crystallite size and the defect levels of ZnO, ensuring good dispersion and conductivity (Toufani et al. 2020). These structural improvements are important for reducing charge recombination in PEC water splitting. However, ball milling is not suitable for synthesizing ZnO/graphene directly into Ni-based substrates especially Ni-foam, as the collision impacts can damage or destroy the integrity of the graphene layer and the conductive metal substrate.

On the other hand, spray pyrolysis offers a simple and scalable method for depositing homogeneous ZnO onto graphene layer. In this method, ZnO precursor solution is atomized into fine droplets and sprayed toward a heated substrate, where rapid solvent evaporation followed by thermal decomposition produces a uniform ZnO/graphene thin film (Flores-Carrasco et al. 2014). The morphology and growth behaviour of the deposited ZnO can be precisely controlled by tuning main parameters, including precursor concentration, spray flow rate, injection or deposition time, and substrate temperature. To date, study has focused on spraying ZnO onto substrate such as graphene/SiO₂ (Ali & Hashim 2015), while on graphene supported on Ni-based substrates remains largely unexplored. These limitations shows that spray pyrolysis is considered not suitable for synthesizing ZnO/graphene on Ni-foam, due to the inability of the precursor penetrate deep into the internal pores, resulting in non-uniform surface coverage, thus reducing the PEC performance.

b. Chemical methods

The hydrothermal method is one of the most commonly used for synthesizing ZnO/graphene on substrates. It is highly preferred due to its ability to precisely control ZnO particle size, morphology, and crystal growth (Basnet & Chatterjee 2020). As

explained in Section 2.5.1, graphene is commonly grown on the Ni substrate, especially Ni-foil and Ni-foam, using CVD. Following this, ZnO nanostructures are deposited on the graphene/Ni substrate via the hydrothermal method, where the graphene/Ni substrate is immersed in a zinc precursor solution and sealed in a stainless-steel autoclave. Then, the autoclave is heated up to 200 °C, generating a high-pressure environment that facilitates the nucleation and growth of ZnO. Various studies have successfully synthesized ZnO/graphene on substrate using this method (Basnet & Chatterjee 2020; Cai et al. 2016; Gadisa et al. 2021; Mohd Shah et al. 2022; Perumal et al. 2019; Rosman et al. 2025). The resulting ZnO morphology is strongly influenced by several hydrothermal parameters, such as type and concentration of ZnO precursor, reaction temperature, reaction time, and pH of the solution during hydrothermal reactions.

Other than hydrothermal method, ZnO can also be deposited on graphene/Ni substrates using the electrodeposition method. This electrochemical method relies on an applied voltage to drive ZnO nucleation and growth and therefore requires a conductive substrate like graphene/Ni. The applied potential must be carefully controlled to match the reduction and deposition behavior of the zinc precursor (He et al. 2022). In addition, CVD has been explored as an alternative way for synthesizing ZnO on graphene. In this method, a zinc-based powder precursor is placed inside a quartz tube next to the substrate coated with graphene, where elevated temperatures promote precursor vaporization and ZnO formation (Madrigal-Monge & Chaves-Villareal 2017). Under controlled conditions, CVD enables the growth of high-quality ZnO films on graphene substrates, hence improved the PEC performance.

2.6.2 Effects on photoanode performance

The formation of ZnO/graphene/Ni photoanode form a synergistic structure that significantly improves light absorption and charge transfer for PEC H₂ production. As mentioned in Section 2.2.1, the PEC performance and STH efficiency is depends on several steps: (1) light absorption: incoming photons create an $e^- - h^+$ pair, (2) $e^- - h^+$ generation (the creation of the excited electron), (3) charge separation and transport (the internal electric field separates the charge carriers), and (4) redox reactions at the

surface of the photoelectrode: the separated charges migrate to the surface to drive the HER and OER (Kindra et al. 2023; Mohd Shah et al. 2021; Tuluhong et al. 2024).

The ZnO/graphene/Ni design is developed to improve these fundamental steps. In terms of light harvesting, Ni-foam promotes multiple light scattering. These properties effect significantly on extending the light absorption region and enabling ZnO to absorb more photons across the visible spectrum (Gadisa et al. 2021; Rosman et al. 2025). With its exceptional conductivity and optical transparency, graphene acts as an efficient electron sink and mediator, thereby suppressing the $e^- - h^+$ pairs recombination and improve the interfacial contact. Furthermore, graphene provides a favourable energy band alignment for chare transfer, offers more active sites for surface reactions, and serves as a protective layer to minimize photocorrosion (Kuang et al. 2020; Mohd Shah et al. 2021). Consequently, the synergistic combination of these materials results in a robust photoanode exhibiting excellent photocurrent density, enhanced charge separation efficiency as well as H_2 production.

a. Improved light absorption

The improvement of light absorption is a critical part of determining the PEC performance, fundamentally depending on the ability of the material to capture the incident photons. Numerous research has demonstrated that coupling ZnO with graphene/Ni-foam significantly improves the light absorption through E_g narrowing and structural light trapping (Gadisa et al. 2021; Wang et al. 2022) By modifying the electronic band structure, it can absorb lower energy photons and utilizing the porous structure of the substrate to induce multiple light scattering (Anuar et al. 2024; Ong et al. 2018).

Regarding E_g modifications, the coupling of ZnO with graphene resulting in a redshift of the absorption edge, effectively narrowing the E_g from the E_g of ZnO (3.37 eV). Men et al. (2016) reported a reduced E_g of 3.18 eV for ZnO/rGO foam, Mohd Shah et al. (2022) and Rosman et al. (2025) observed E_g of 3.22 eV and 3.06 eV (Figure 2.18 (a)), respectively, for ZnO/3D graphene/Ni-foam. The reduction of E_g also attributed to the introduction of intermediate energy levels on the ZnO. Gadisa et al.

(2019) demonstrated that C-doping on ZnO, introduced new energy states that lowered the E_g to 3.18 eV (Figure 2.18 (b)).

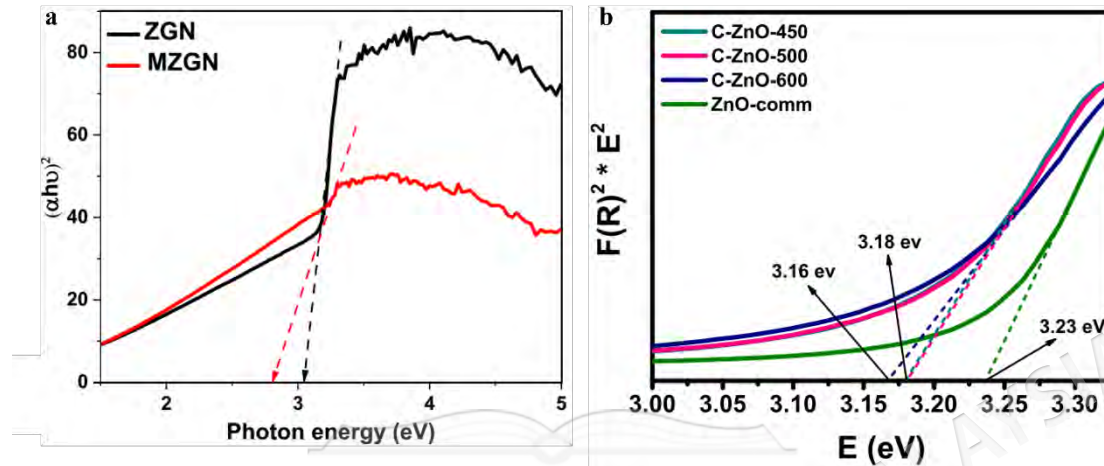


Figure 2.18 Tauc plots of (a) ZnO/graphene/Ni-foam (ZGN) and (b) C-doped ZnO (C-ZnO-450).

Source: Gadisa et al. (2019) and Rosman et al. (2025)

In terms of morphology, the porous structure of substrate and the morphology of ZnO plays an important role in light absorption. He et al. (2022) showed that coating ZnO nanosheets with ultrathin 3DrGO produces a rougher surface, extending light absorption into the visible region (400 – 800 nm). Furthermore, the highly porous nature of the Ni-foam provides a higher surface area for uniform ZnO deposition. This porous substrate enhances light interaction through multiple light scattering within the pores. Additionally, the additional active sites provided by the ZnO nanorods results in excellent absorption capabilities compared to ZnO grown on flat substrates (Cai et al. 2016; Gadisa et al. 2021; Mohd Shah et al. 2022).

b. Enhanced charge transfer

To understand PEC performance, the first essential step is the photoactive material must absorb photons to generate excited electron. Then, these photogenerated electron transfer from the CB to the surface to produce H_2 , while the holes remain at the VB to drive the oxidation (Kindra et al. 2023; Tuluhong et al. 2024). However, ZnO is limited by the rapid recombination of photogenerated $e^- - h^+$ pairs. To overcome this, coupling ZnO with graphene and a Ni-based substrate is an effective strategy, as graphene acts

as a highly conductive pathway for fast electron transport, while the Ni substrate further improves electrical conductivity and mechanical support (Liu et al. 2017). The synergistic structure suppresses recombination and enhances charge transfer, thereby improving the PEC performance of the ZnO-based photoanode.

This strategy is supported by several works. For instance, Men et al. (2016) showed that ZnO/rGO foam decorated with ZnO nanorods increased the current density to 0.27 mA/cm^2 , higher than ZnO (0.007 mA/cm^2) at 1.00 V in 0.50 M Na_2SO_4 (Figure 2.19 (a)). Similarly, He et al. (2022) synthesized a ZnO/3DrGO on FTO glass and achieved photocurrent density of 1.43 mA/cm^2 at 1.23 V vs RHE, confirming that 3D graphene boosts the charge carrier density and significantly enhances PEC performance (Figure 2.19 (b)). This enhancement was further supported by EIS analysis, where the ZnO/3DrGO exhibited a lower R_{ct} than pure ZnO, indicating more efficient interfacial charge transfer and suppressed charge recombination. Furthermore, the ZnO/3DrGO shows a 36.8% increase in photocurrent density after 2 hours, highlighting the beneficial role of 3D graphene in improving both PEC activity and stability.

However, the results are even more impressive when using conductive Ni-foam substrate. For instance, Gadisa et al. (2021) demonstrated that carbon-modified ZnO grown on Ni-foam (ZnO-C/NF) reached 100 mA/cm^2 at 0.90 V in 1 M KOH electrolyte, outperforming the 30 mA/cm^2 achieved by ZnO/Ni-foam without carbon materials (Figure 2.19 (c)). Furthermore, the ZnO-C/NF exhibited good stability, maintaining approximately 60% of its initial current density after 8 hours of continuous light irradiation. Besides, Rosman et al. (2025) reported a photocurrent density of 83 mA/cm^2 for ZnO/graphene/Ni-foam (ZGN) at 1.00 V vs Ag/AgCl in 0.50 M Na_2SO_3 electrolyte. Interestingly, the onset potential of this ZGN shifted toward 0 V, attributed to the excellent conductivity of the Ni-foam substrate (Figure 2.19 (d)). For stability testing under continuous illumination, the ZGN retained about 75% of its initial current density after 0.50 hours. These results highlight the beneficial role of carbon incorporation in enhancing both the PEC performance and stability of ZnO-based photoanodes. Although Rosman et al. (2025) showed the excellent synergistic effects of combining ZnO with graphene/Ni-foam, the integrated graphene layer was not systematically optimized in terms of the thickness or loading. This leaves a critical

research gap regarding how precise interfacial control contributes to the resulting PEC performance. Consequently, the current study comprehensively explored this limitation by synthesizing high-quality, optimized graphene layers using CVD.

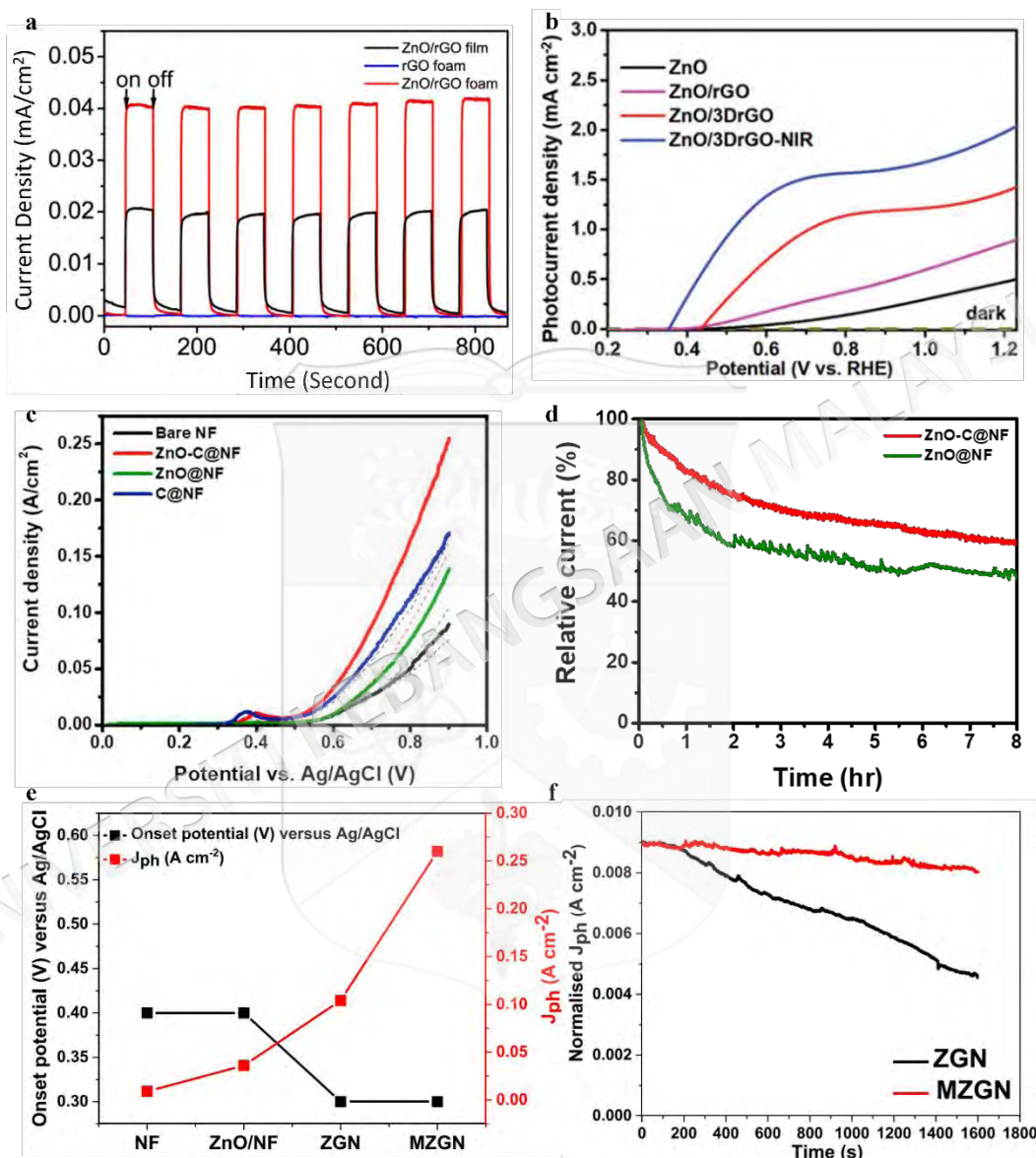


Figure 2.19 PEC performance of the synthesized photoanodes: (a) ZnO/rGO, (b) ZnO/3DrGO, (c) ZnO-C@NF, and (d) ZGN.

Source: Gadisa et al. (2021), He et al. (2022), Men et al. (2016) and Rosman et al. (2025)

This improvement in efficiency is further confirmed by Nyquist plots, where the smaller arc semicircle diameters indicate outstanding charge transfer efficiency (Gadisa et al. 2019; Rosman et al. 2025). Each material in the ZnO/graphene/Ni-foam plays an important role in achieving high PEC performance. Graphene enhances charge transfer through its zero-band gap nature, enabling rapid electron transport and effectively suppressing $e^- - h^+$ recombination. The strong interfacial contact between ZnO and graphene further improves charge separation efficiency (Desai et al. 2019). Meanwhile, the Ni-foam substrate provides excellent electrical conductivity and a highly porous 3D structure, allowing efficient charge transfer. In conclusion, the synergistic combination of graphene and Ni-foam serves as an efficient electron mediator and conductive channels, greatly enhancing charge transfer and improving the PEC performance of ZnO/graphene/Ni-foam photoanodes (Anuar et al. 2024; Liu et al. 2017). However, despite these promising characteristics, no reported work has demonstrated H_2 production using ZnO/graphene/Ni-based photoanodes (Table 2.3).

Table 2.3 Summary of recent research on ZnO/graphene/Ni for PEC H₂ production.

Material	Method	Electrolyte	Photocurrent density (mA/cm ²)	Onset potential (V vs Ag/AgCl)	Stability	Reference
ZnO	-	0.50 M Na ₂ SO ₄	0.007	-	-	(Men et al. 2016)
ZnO/rGO foam	Hydrothermal	0.50 M Na ₂ SO ₄	0.27 at 1.00 V vs Ag/AgCl	-	-	(Men et al. 2016)
ZnO/3DrGO/FTO	Electrodeposition	-	1.43 at 1.23 V vs RHE	0.42	Improve 36.8% from the initial photocurrent density after 2 hours	(He et al. 2022)
C/Ni-foam	Hydrothermal	1 M KOH	10 at 0.90 V vs RHE	0.38	-	(Gadisa et al. 2021)
ZnO/Ni-foam	Hydrothermal	1 M KOH	30 at 0.90 V vs RHE	0.50	<50% current density retained after 8 hours	(Gadisa et al. 2021)
ZnO/C/Ni-foam	Hydrothermal	1 M KOH	100 at 0.90 V vs RHE	0.40	Maintained >60% of its initial current density after 8 hours	(Gadisa et al. 2021)
ZnO/G/Ni-foam	CVD, Hydrothermal	0.50 M Na ₂ SO ₃	83 at 1.00 V vs Ag/AgCl	0.30	Maintained about 75% after 0.50 hours	(Rosman et al. 2025)
ZnO/Ni-foam	Hydrothermal	0.50 M Na ₂ SO ₃	40 at 1.00 V vs Ag/AgCl	0.40	-	(Rosman et al. 2025)

Although EIS is widely used to evaluate charge transfer efficiency in PEC systems, it primarily provides indirect information through equivalent circuit fitting. A smaller semicircle diameter in the Nyquist plot is generally associated with lower R_{ct} and more efficient interfacial charge transport (Bredar et al. 2020; Mei et al. 2018). However, EIS alone cannot directly identify the specific charge transfer pathway, determine the origin of charge recombination, or reveal the energy level alignment at the photoelectrode-electrolyte interface. Therefore, Mott-Schottky analysis provides additional insights into the electronic properties of the photoelectrode, including the flat-band potential, donor density, and semiconductor conductivity type. These parameters are important for understanding band bending and the driving force for charge separation at the interface (Hankin et al. 2019; Sivula 2021). Nevertheless, Mott-Schottky measurements do not directly quantify charge transfer kinetics or recombination rates. Consequently, EIS and Mott-Schottky analyses are complementary techniques, where EIS investigates R_{ct} while Mott-Schottky analysis elucidated the electronic structure governing charge separation and transport.

2.6.3 Evaluation of the charge transfer mechanism

Evaluating the charge transfer mechanism is important for understanding how ZnO/graphene/Ni-based photoanodes improve PEC performance. In this system, the efficiency of charge transfer is significantly influenced by the interfacial interactions between ZnO, graphene, and Ni substrate. To examine this, several experimental characterization techniques are used (described in detail in Chapter III), such as UV-Vis analysis, LSV, CA, EIS, Mott-Schottky analysis, and H_2 production measurements. It will provide valuable insights on charge transfer resistance, charge carrier density, light absorption, and PEC behavior. These findings help to explain how graphene and Ni facilitate rapid electron transfer while reducing recombination losses. To further support these findings, DFT calculations are performed to investigate charge distribution, electronic structure, and the interfacial interactions at the atomic scale. By combining the experimental results with theoretical calculations, the charge transfer mechanism can be validated, providing a deeper understanding of the synergistic roles of ZnO, graphene, and Ni in enhancing PEC H_2 production.

a. Experimental

To understand the charge transfer mechanism of ZnO/graphene/Ni photoanode, the results of optical, structural, and electrochemical characterization is required. This is because, each characterization was evaluated specific parameters, from light absorption to interfacial kinetics that validated the PEC performance. Table 2.4 summarizes the characterization techniques used in this study, along with the specific parameters evaluated.

Table 2.4 Summary of characterization techniques to evaluate charge transfer and electrochemical performance of ZnO/graphene/Ni photoanode.

Characterization technique	Parameters evaluated	Role in charge transfer analysis	References
UV-Vis Spectroscopy	- Absorption edge - Band gap energy (eV)	Estimates light absorption ability. A redshift or blueshift enhanced visible absorption suggests improved potential for current generation.	(Das et al. 2020)
PEC measurements (LSV, CA)	- Photocurrent density (mA/cm²) - E_{onset} (mA/cm²) - Stability (mA/cm²/s)	Determines the overall efficiency of charge transfer. A higher photocurrent and lower onset potential indicate effective charge separation.	(Sazali et al. 2024)
EIS	- Nyquist plot - Charge transfer resistance (Ω)	Measures charge transfer resistance at the photoelectrode-electrolyte interface. A smaller semicircle indicates faster electron mobility and lower resistance.	(Mohamed et al. 2019)
Mott-Schottky Analysis	Charge carrier density (1/cm³)	Identifies semiconductor type (p- or n-type) and reveals how graphene and Ni improve band alignment and charge carrier density.	(Adris et al. 2024; Rosman et al. 2025)
GC	- H₂ production (mmol/s) - Faradaic efficiency (%)	Quantifies actual H ₂ evolution and compare the measured gas from the experimental with the theoretical value calculated from the photocurrent density and determine the Faradaic efficiency.	(Ahmed & Dincer 2019)

Overall, these characterization results provide a comprehensive understanding of the charge transfer mechanism. It demonstrates how graphene and Ni enhance the light absorption, facilitating electron transport, reducing the recombination losses, and improving the PEC performance of ZnO-based photoanodes.

b. Density Functional Theory

The evaluation of charge transfer using computational methods, like Density Functional Theory (DFT), is widely utilized to study the charge transfer mechanism at the ZnO/graphene/Ni interface. DFT provides valuable atomic-level insights into how graphene and Ni improve the performance of ZnO photoanodes (Geng et al. 2013). From these computational calculations, the electronic properties such as density of states, interfacial interaction, binding energy (E_b), charge density differences, and band bending alignment can be predicted, which directly influence PEC activity (Fathzadeh et al. 2020). Moreover, the computational results play an important role in supporting the experimental findings by confirming the favourable electron transport pathways.

Previous studies have investigated graphene interactions with various metal substrates (Christian et al. 2017; Hamada & Otani 2010; Zhao et al. 2011; Zheng et al. 2013). Among the metals, graphene exhibits the strongest interaction with Ni, particularly with the Ni (111) surface, compared to Cu, Ag, Au, Pd and Pt. This strong interaction is attributed to the small lattice mismatch between graphene and Ni (111), which allow graphene to chemisorb onto the Ni (111) surface (Christian et al. 2017). As shown in Figure 2.20, several configurations for graphene on Ni (111) have been reported, such as (i) bridge-fcc, (ii) bridge-hcp, (iii) bridge-top, (iv) fcc-hcp, (v) top-fcc, and (vi) top-fcc. Among these, the top-fcc and bridge-top configurations are the most stable, lying within the accuracy of DFT when considering the significant contributions of vdW forces (Christian et al. 2017; Zhao et al. 2011).

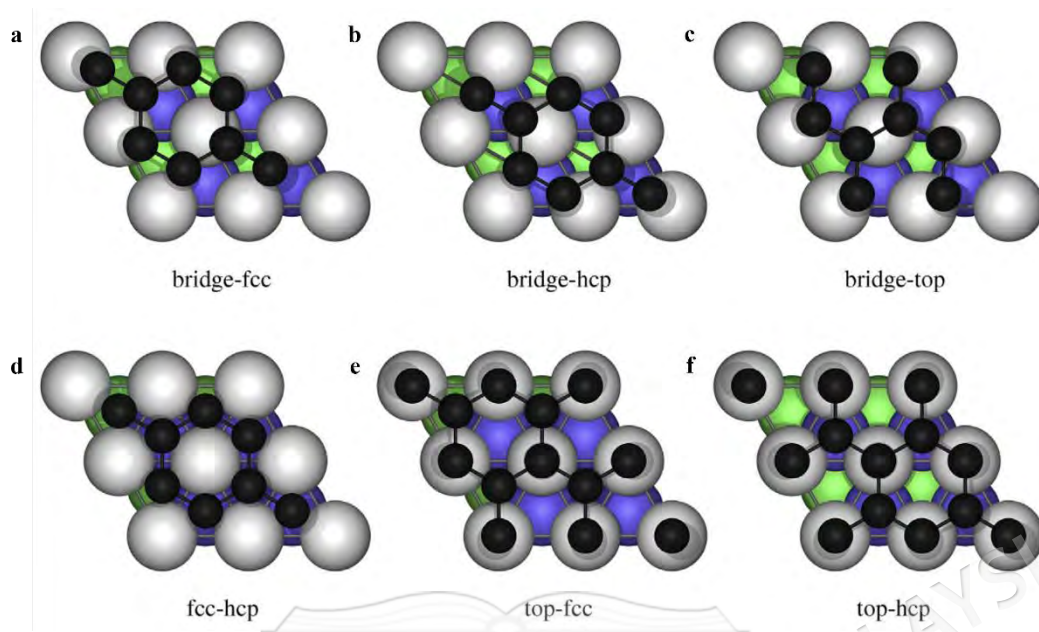


Figure 2.20 Six different configurations of graphene on a Ni substrate. The Ni (111) surface layers are presented in light grey (top layer), blue (second layer), and green (third layer), with black for carbon atoms.

Source: Christian et al. (2017)

For ZnO-graphene interface, ZnO can exist in different surface terminations due to the presence of Zn and O atoms. These terminations are commonly categorized as (i) polar surface (Zn-terminated ZnO and O-terminated ZnO) and (ii) nonpolar surface (Figure 2.21) (Hewlett & McLachlan 2016). Geng et al. (2013) reported the equilibrium interlayer distances between ZnO and graphene is 2.55 Å and 2.89 Å for Zn-terminated and O-terminated ZnO, respectively, with the E_b of -4.13 eV and -3.21 eV, respectively. These values indicate that the vdW interactions at the ZnO-graphene interface are relatively weak (Fathzadeh et al. 2020; Geng et al. 2013). In addition, Fathzadeh et al. (2020) showed that electron transfer from ZnO to graphene for Zn-terminated ZnO, while the direction of electron movement is opposite for O-terminated and nonpolar surface of ZnO, where electrons transferred from graphene to ZnO. It shows that the charge transfer mechanism strongly depends on the ZnO surface termination.

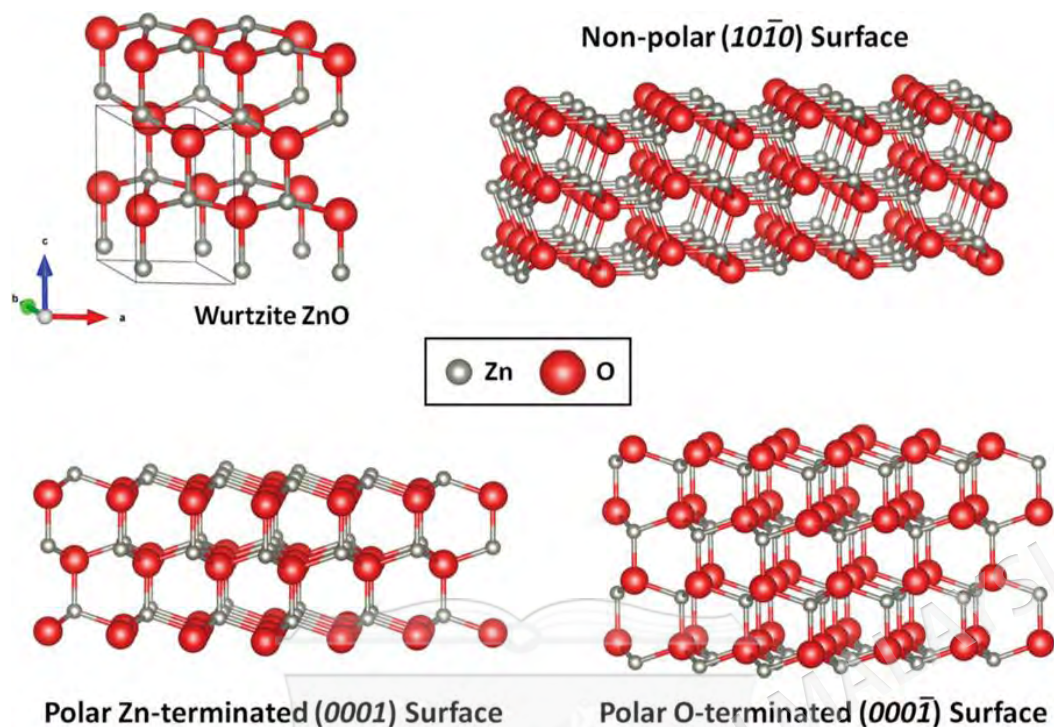


Figure 2.21 Schematic illustration of the wurtzite ZnO crystal structure, with the non-polar and polar (Zn- and O-terminated) surfaces.

Source: Hewlett & McLachlan (2016)

2.7 CONCLUSION

Based on the literature review, although tandem PEC systems can achieve high STH efficiency by overcoming the voltage limitations of single-absorber, the PEC performance is still fundamentally limited by the efficiency of each photoelectrode component. The PEC reaction starts with OER at the photoanode, then electrons are transferred to the photocathode to perform HER. If the photoanode is not efficient, it becomes the main drawback of the entire system. This limitation occurs because OER is a slow kinetic reaction that involves four-electron that requires a high overpotential and often suffers from stability issues.

In this study, ZnO is selected as the photoanode material. Although ZnO offers several advantages, its performance is limited by poor charge transfer efficiency and rapid charge recombination. Various strategies have been explored to overcome these issues, and incorporating carbon-based materials like graphene has shown significantly improve the PEC performance due to graphene's excellent electrical conductivity and

ability to facilitate fast electron transport. The modification becomes even more effective when combining Ni-based substrates, specifically Ni-foam, provides a highly porous structure with abundant active sites, which significantly enhances PEC activity.

Therefore, this study focuses on the development of ZnO/graphene/Ni photoanodes to further improve the PEC performance and stability of single-absorber systems. Although several studies have investigated ZnO/graphene and graphene/Ni interfaces individually, research on the combination of ZnO/graphene/Ni configuration remains limited. In addition, most existing studies report only photocurrent performance without determining the H₂ production. Thus, this work aims to investigate how the combined effects of ZnO, graphene, and Ni influence the photocatalytic properties, PEC performance, charge transfer pathway, and H₂ production of ZnO/graphene/Ni.



CHAPTER III

RESEARCH METHODOLOGY

3.1 INTRODUCTION

This chapter provides a detailed explanation of the research methods used in this study. It can be divided into two sections: (i) the experimental work including the selection of substrate, synthesis processes, physicochemical and photoelectrochemical (PEC) characterizations, as well as sample preparation for PEC measurements, and (ii) the computational study, which focuses on structural optimization using Density Functional Theory (DFT).

3.2 LIST OF CHEMICALS

The list of chemicals used in this study is listed in Table 3.1.

Table 3.1 List of chemicals used.

Chemical	Molecular formular	Purity (%)	Brand
Nickel foam (sheet): 4 x 6 cm Thickness: 0.16 cm	-	90 – 98	TOB
Nickel foil Thickness: 0.025 cm	-	99.99	Sigma Aldrich
Acetone	C ₃ H ₆ O	Analytical grade	R & M
Ethanol	C ₂ H ₅ OH	Analytical grade	R & M
Deionized (DI) water	H ₂ O	99	Evoqua Water Technologies
Argon	Ar	99.99	Alpha Gas Solution
Hydrogen	H ₂	10/90 (H ₂ /Ar)	SIG

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Methane	CH ₄	50/50 (CH ₄ /Ar)	Alpha Gas Solution
Zinc nitrate hexahydrate	Zn(NO ₃) ₂ ·6H ₂ O	98	Sigma Aldrich
Sodium hydroxide	NaOH	≥ 97	Sigma Aldrich
Sodium sulfite	Na ₂ SO ₃	≥ 98	Sigma Aldrich
Potassium chloride	KCl	-	HACH
Silver/silver chloride	Ag/AgCl	-	HACH

3.3 LIST OF INSTRUMENTATION

The list of instrumentations used in this study is tabulated in Table 3.2.

Table 3.2 List of instruments used.

Instrument	Description	Function
Ultrasonic bath sonicator	Brand: Elma Model: Elmasonic Select 100	To clean the Ni-foam
Quartz tube	50 OD x 44 ID x 450 L (mm)	To synthesis graphene/Ni-foam via CVD method
Tube furnace	Brand: MTI corporation Model: OTF-1200X	To synthesis graphene/Ni-foam via CVD method
Stainless-steel autoclave with Teflon-lined	50 mL	To synthesis ZnO/graphene/Ni-foam photoanode via hydrothermal method
Box furnace	Brand: Carbolite Gero Model: CWF 1200	To synthesis ZnO/graphene/Ni-foam photoanode via hydrothermal method
Raman spectroscopy	Brand: Thermo Scientific Model: DXR2xi	To study the characteristics of graphene
Field emission scanning electron microscope (FESEM)	Brand: ZEISS Model: SUPRA 55VP	For morphological study of the samples
X-ray diffraction (XRD)	Brand: Bruker Model: D8 Advance	For structural and crystallinity study of the samples
Ultraviolet-visible spectroscopy (UV-Vis)	Brand: Perkin Elmer Model: Lambda 950	To investigate the light absorption properties of the samples
X-ray photoelectron spectroscopy (XPS)	Brand: Kratos Model: Axis Ultra DLD	To analyze the surface chemistry and the bonding mode of the samples

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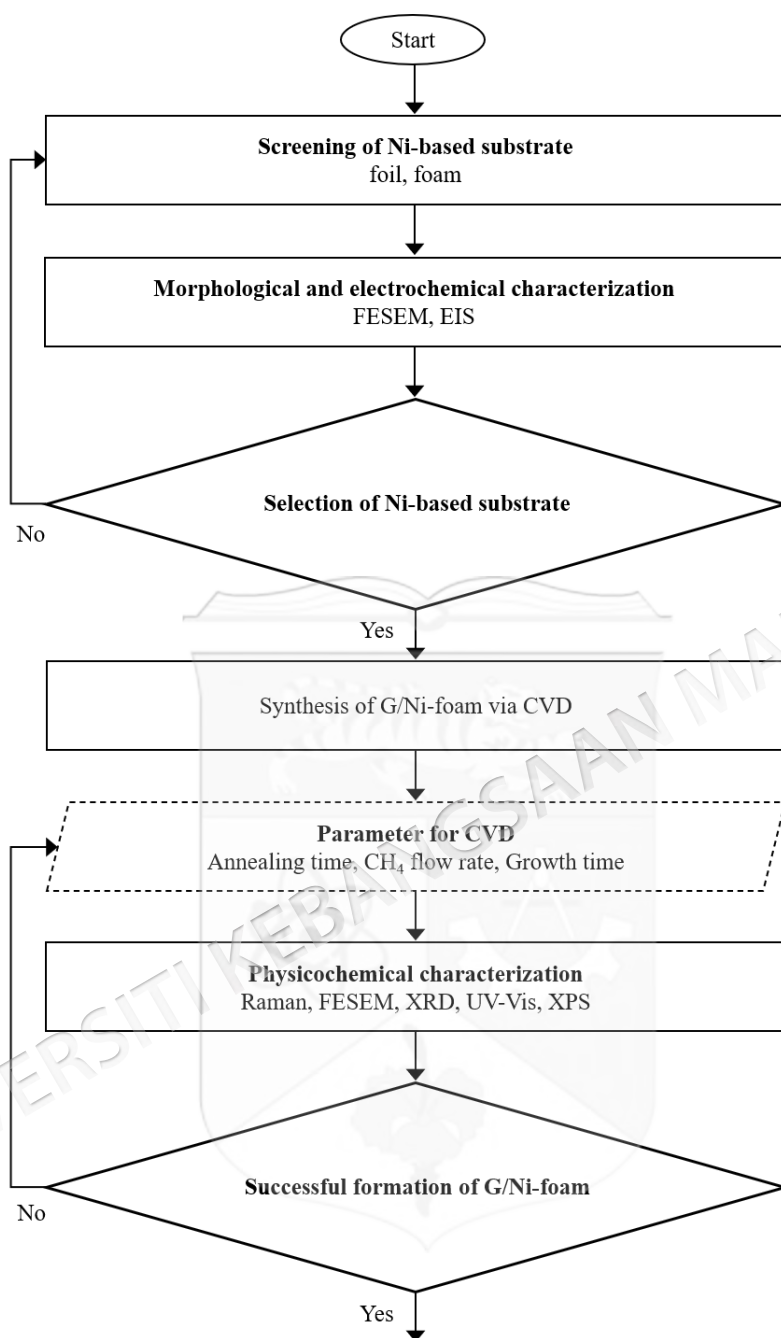
... continuation

Potentiostat	Brand: Corrtest Model: CS350M	For electrochemical and PEC testing
Gas chromatography (GC)	Brand: Agilent Model: 7890A	To collect H ₂ gas
STATE-Senri code	Permission from The University of Osaka, Japan	For DFT study

3.4 FLOWCHART OF METHODOLOGY

The overall workflow of this study is represented in Figure 3.1. It starts with the selection of Nickel (Ni) substrate, followed by graphene growth on the Ni substrate using Chemical Vapor Deposition (CVD) method. Three parameters are systematically controlled, followed by physicochemical characterization. The best graphene/Ni sample will be selected to be decorated with ZnO via the hydrothermal method by modifying reaction temperature. Subsequently, the resulting photoelectrodes are examined through physicochemical and PEC characterizations. The best ZnO on graphene/Ni photoelectrode will be selected for further analysis for stability and hydrogen (H₂) production rate. All experimental procedures were carried out in triplicate for every sample set to ensure reproducibility and consistency.

Simultaneously, computational designs are carried out to elucidate the charge transfer mechanism for ZnO/graphene/Ni using DFT with the Simulation Tool for Atom Technology (STATE)-Senri code. Two ZnO surface terminations: zinc-terminated (Zn-terminated) and oxygen-terminated (O-terminated) are studied, along with two interface orientations of graphene/Ni: Top-fcc and Bridge-top. Finally, the charge transfer mechanism of ZnO/graphene/Ni photoelectrode will be elucidated using both experimental and theoretical approach.



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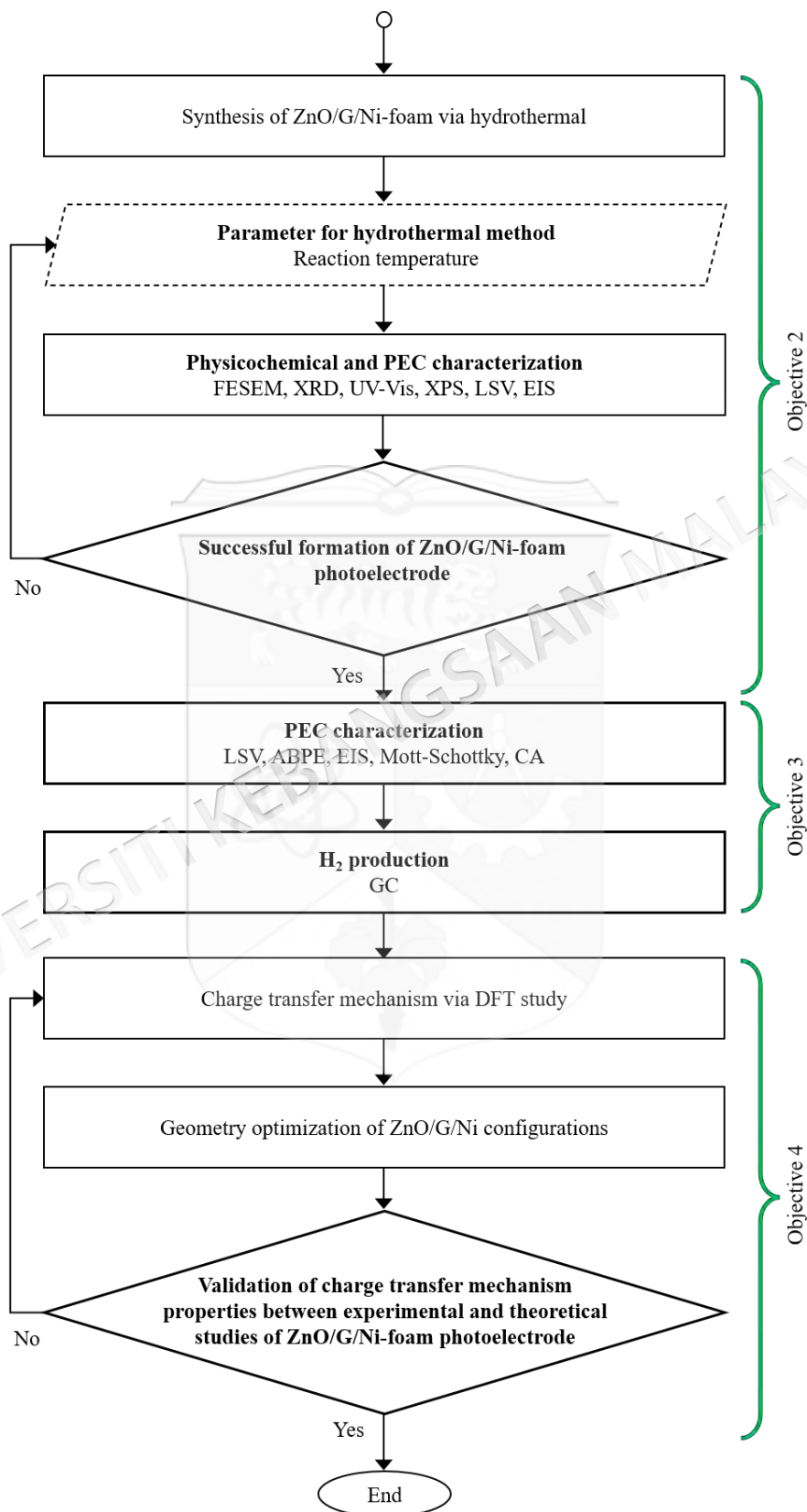


Figure 3.1 Flowchart of this study.

3.5 SUBSTRATE SELECTION AND MATERIAL SYNTHESIS

This section describes the overall procedures involved in substrate preparation and synthesizing the photoelectrode materials. The synthesis begins with the growth of graphene on Ni-based substrate using CVD method, followed by the deposition of ZnO through a hydrothermal process to form ZnO/graphene/Ni photoelectrode. Each step was carefully designed to enhance the surface area, electronic and photocatalytic properties, thereby improving the overall PEC performance of the resulting photoelectrode. The detailed experimental procedures and synthesis parameters are described in the following sections.

3.5.1 Substrate selection

As stated in Chapter I, the selection of an appropriate substrate for graphene growth is crucial. Therefore, screening of Ni-based substrates was performed prior to the growth process. The procedure was referred to Cai et al. (2016) and Men et al. (2016), where the Ni-@ substrates (@ denotes both foil and foam) will be cut into 1.50 cm x 1.50 cm pieces, as illustrated in Figure 3.2. Then, it will go through ultrasonic cleaning using acetone, ethanol, and deionized (DI) water for 10 minutes each to remove the impurities. Then, each of them will be dried with nitrogen blow for 5 minutes. Before proceeding with the CVD method, morphological and electrochemical characterization will be conducted on the Ni-@ substrates. FESEM will be used to investigate surface morphology, while EIS will be employed to examine the electrical properties. Then, the best Ni substrate will be chosen to proceed with the subsequent synthesis steps, which involve tuning three CVD parameters: annealing time, CH₄ flow rate, and growth time.

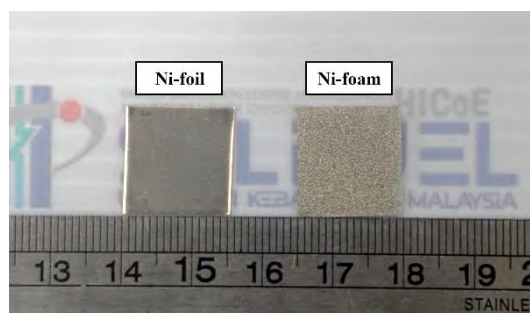


Figure 3.2 Digital photograph of Ni-foil and Ni-foam.

3.5.2 Material synthesis using Chemical Vapor Deposition (CVD)

This study emphasizes the synthesis of graphene/Ni substrates via CVD method, systematically controlling three main parameters: annealing time (x), CH_4 flow rate (y), and growth time (z). These CVD parameters were adapted from previous research that using CVD for graphene growth on substrates (Bello et al. 2013; Cai et al. 2016; Rosman et al. 2021; Trinsoutrot et al. 2014). In this study, Ni-foam was selected as the most suitable substrate for further investigations. The procedure for the initial steps is the same as mentioned in Section 3.5.1. After the drying process, the Ni-foam was placed at the center of the quartz tube (50 OD x 44 ID x 450 L in mm). Then, the tube furnace gradually heated from 25 °C to 1000 °C for 50 minutes (heating rate = 20 °C/minute) under continuous flow of Ar (100 sccm) and H_2/Ar (400 sccm) conditions. The experimental setup for the CVD is shown in Figure 3.3.

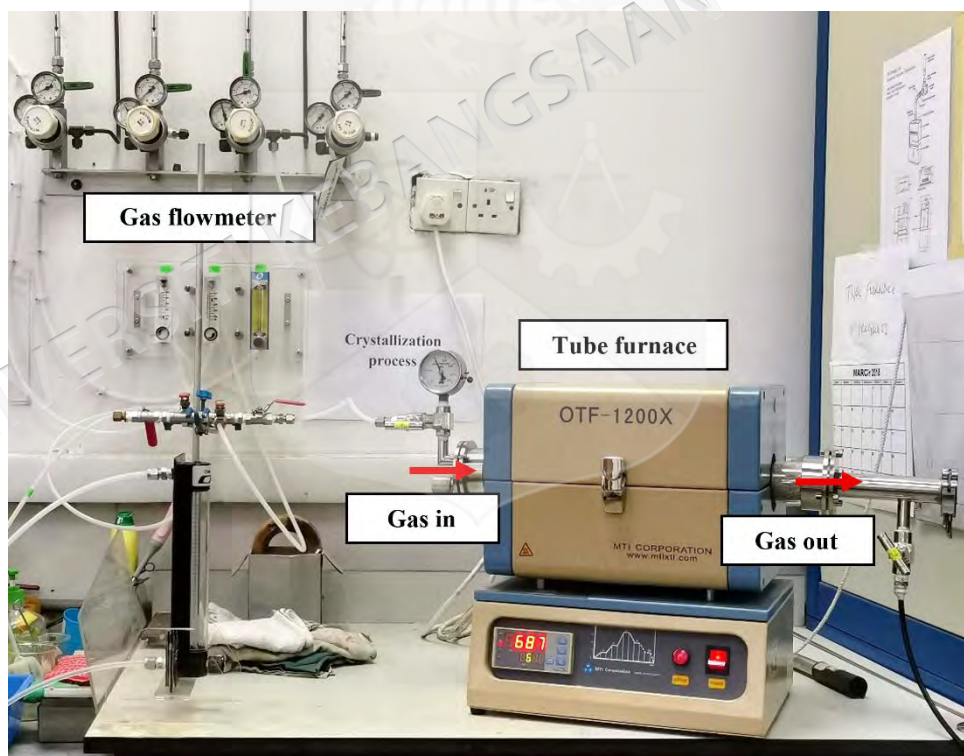


Figure 3.3 The experimental setup for CVD.

The overall temperature profile for the CVD method is illustrated in Figure 3.4. The initial step of the synthesis focused on choosing the annealing time to grow graphene on Ni-foam. Annealing was conducted under Ar and H₂/Ar gas flow, with the annealing time varied from $x = 0, 20$ to 60 minutes. Since most studies used 30 to 40 minutes as the ideal annealing time to prepare the Ni surface for graphene growth (Ibrahim et al. 2015; Jin et al. 2014), the annealing time of 10 minutes was excluded from further study. For graphene growth on Ni-foam, CH₄ (20 sccm) was supplied as the carbon source together with Ar (150 sccm) and H₂/Ar (250 sccm) for 30 minutes. After that, the temperature of the quartz tube will be rapidly cooled in Ar (500 sccm) until it reaches room temperature, leading to the formation of graphene/Ni-foam.

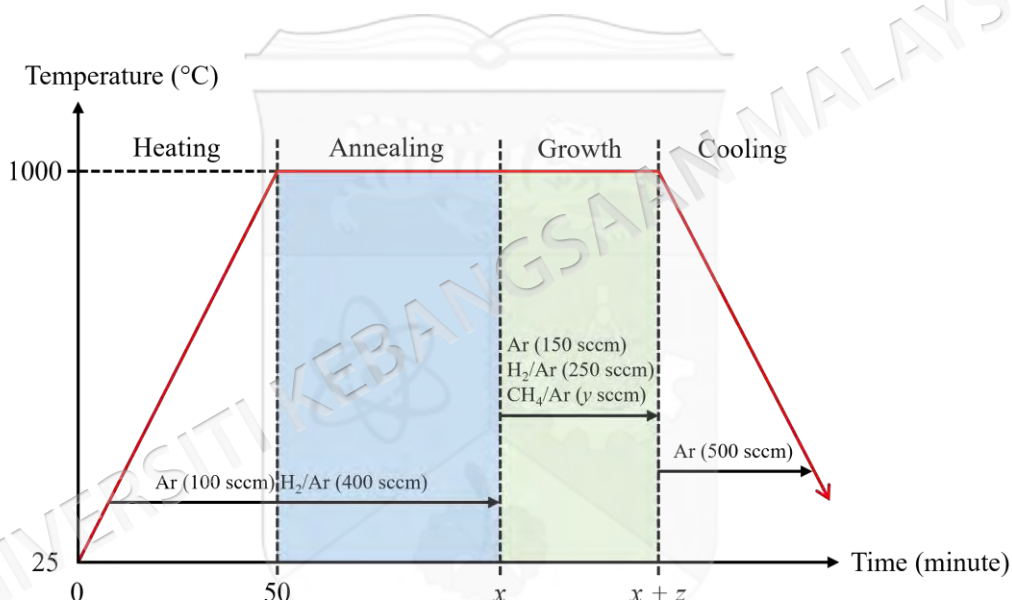


Figure 3.4 The overall temperature profile for graphene growth via CVD.

The second step involved determining the suitable CH₄ flow rate for achieving the thinnest possible graphene layer that fully covered the Ni-foam surface. Using the best annealing time of 50 minutes identified in the previous step, the CH₄ concentration was systematically adjusted across $y = 0$ to 30 sccm, while maintaining Ar and H₂/Ar flows for 30 minutes of growth. Subsequently, the quartz tube was rapidly cooled to room temperature with Ar (500 sccm) before the resulting graphene/Ni-foam samples were obtained.

Finally, the focus shifted to find the best graphene growth time. The best CH₄ concentration (10 sccm) determined in the prior step was employed, alongside Ar (150 sccm) and H₂/Ar (250 sccm) flows. The growth time was controlled between $z = 0$ and 30 minutes. As with the previous steps, the quartz tube was rapidly cooled to room temperature using Ar (500 sccm) upon completion, yielding the final graphene/Ni-foam samples. Through systematic adjustment of the CVD parameters, successful graphene synthesis was achieved under optimal conditions of 50 minutes annealing time, 10 sccm CH₄ flow rate, and 20 minutes growth time. These modified parameters produced a uniform graphene layer, well-adhered graphene layer with enhanced structural integrity and surface coverage on Ni-foam.

Before proceeding with the hydrothermal method, a series of physicochemical characterizations were performed to confirm the presence of graphene and to explore the morphology and structural properties of the graphene/Ni-foam. Raman analysis is used to study the fundamental properties and vibrational modes of graphene, FESEM is utilized to determine the surface morphology, including coverage area, thickness and the quality of the graphene layer, XRD is used to determine the crystallographic structure and crystallinity, UV-Vis spectroscopy is employed to evaluate the light absorption properties and XPS analysis to investigate the chemical bonding of the graphene/Ni-foam. Section 3.7 described the detail procedure about these characterizations and the best CVD parameters that influence the successful growth of graphene on Ni-foam will be chosen to be decorated with ZnO, as described in next section.

3.6 SYNTHESIS OF ZnO ON GRAPHENE/NICKEL FOAM PHOTOELECTRODE VIA HYDROTHERMAL METHOD

The preparation of ZnO on graphene/Ni-foam (ZnO/graphene/Ni-foam) via hydrothermal method was carried out using zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) as a ZnO precursor. The hydrothermal reaction time (8 hours) (Holi et al. 2019; Idiawati et al. 2017; Lu et al. 2017), ZnO precursor concentration (0.50 M) (Mohan et al. 2020), and reactant pH (4) (Baruah & Dutta 2009) were fixed while selecting the hydrothermal reaction temperature. This approach was chosen because temperature serves as the primary thermodynamic parameter controlling the crystalline nucleation and structural

growth kinetics of hydrothermal ZnO. Two separate solutions were prepared. In the first solution, 4.46 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL of DI water and stir for 30 minutes at 200 rpm. To transform the ZnO precursor to ZnO, reducing agents like NaOH is needed to promote the growth of ZnO (Biron et al. 2020; Wang et al. 2015).

Therefore, in the second solution, 5 M of NaOH was prepared in DI water and stir for 30 minutes at 200 rpm. Then, three drops of NaOH will be added to the first solution under continuous stirring. This mixture is transferred to a 50 mL Teflon-lined stainless steel hydrothermal autoclave before immersing the graphene/Ni-foam. The sample is heated in the box furnace for 8 hours at various hydrothermal reaction temperatures: 150 °C, 180 °C, 190 °C, 200 °C and 220 °C. The selection of the hydrothermal reaction temperature was modified from previous studies by Mohan et al. (2020) and Ejsmont & Goscianska (2023), to ensure the successful growth of ZnO directly onto the graphene/Ni-foam. After cooling, the samples are rinsed with DI water and heated to 450 °C for 1 hour at a rate of 5 °C/minute. Finally, the ZnO/graphene/Ni-foam photoelectrode is obtained. The steps are illustrated in Figure 3.5.

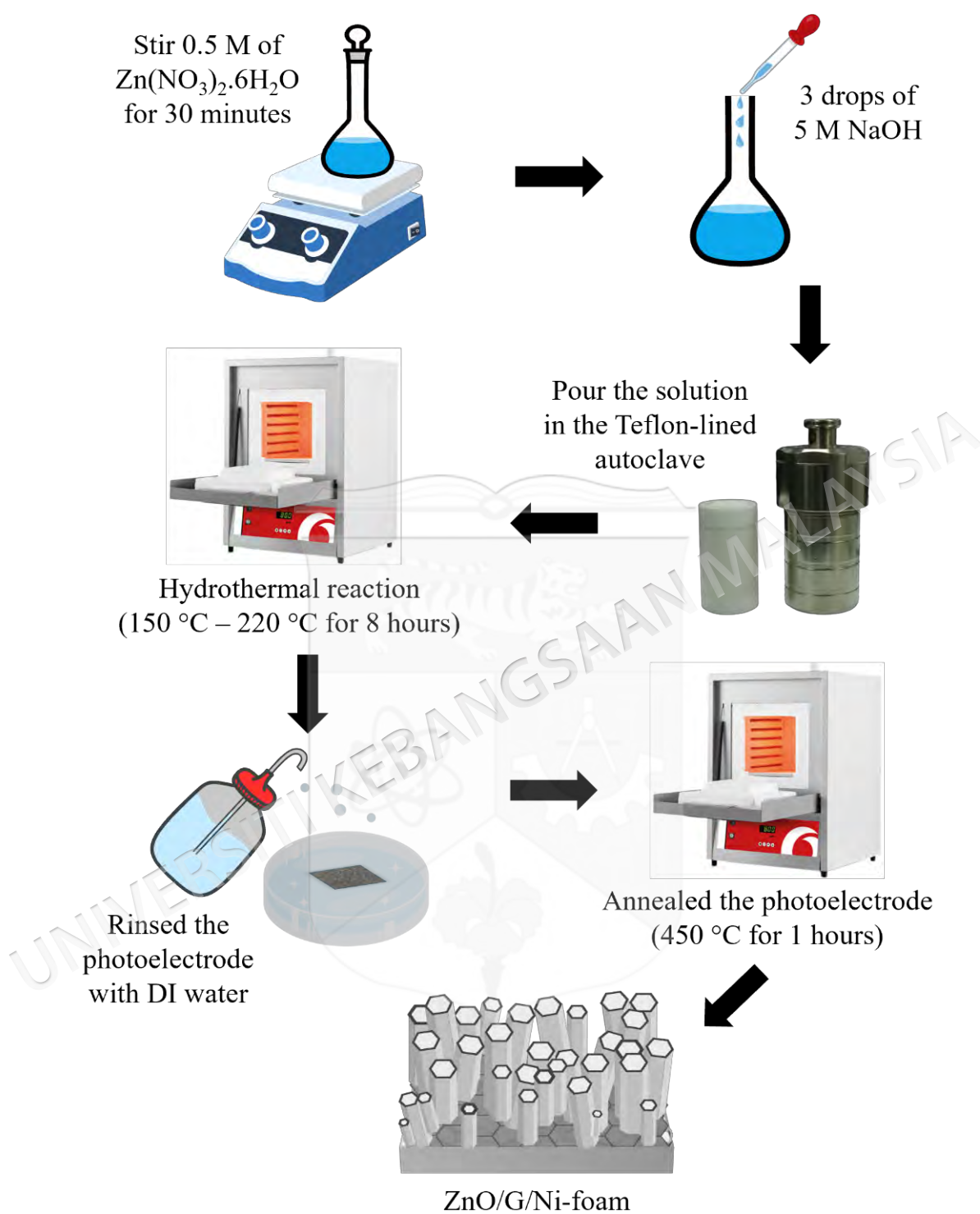


Figure 3.5 Schematic illustration for hydrothermal method to grow ZnO.

3.7 PHYSICOCHEMICAL CHARACTERIZATION

Upon completion of the synthesis process, all samples were characterized using various analytical techniques to investigate the influence of parameters applied in both steps: the growth of graphene on Ni-foam and the deposition of ZnO on graphene/Ni-foam photoelectrode. The success of the synthesis was visually confirmed, as can be seen in Figure 3.6, where the Ni-foam displayed a color change from grey to black after graphene growth and to a greying-white color after ZnO deposition. The characterization techniques and corresponding analysis procedures are described in the following sections.

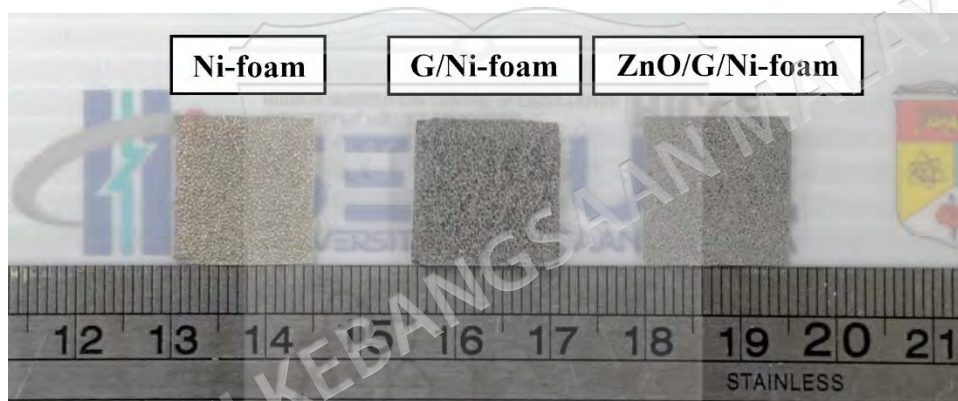


Figure 3.6 Photo images of samples.

3.7.1 Intrinsic properties of graphene

The intrinsic properties of graphene grown on Ni substrate, like the vibration modes, quality, and layer thickness, were analyzed using Raman spectroscopy at i-CRIM Centralized Laboratory, Universiti Kebangsaan Malaysia (UKM). This technique is a non-destructive technique that involves irradiating a sample with 532 nm laser to induce Raman scattering. To make sure the graphene layer was grown uniformly across Ni, results were collected from three different spots on each sample. The classification of the graphene layer was determined based on the intensity ratio of the characteristic Raman peaks, as shown in Figure 3.7.

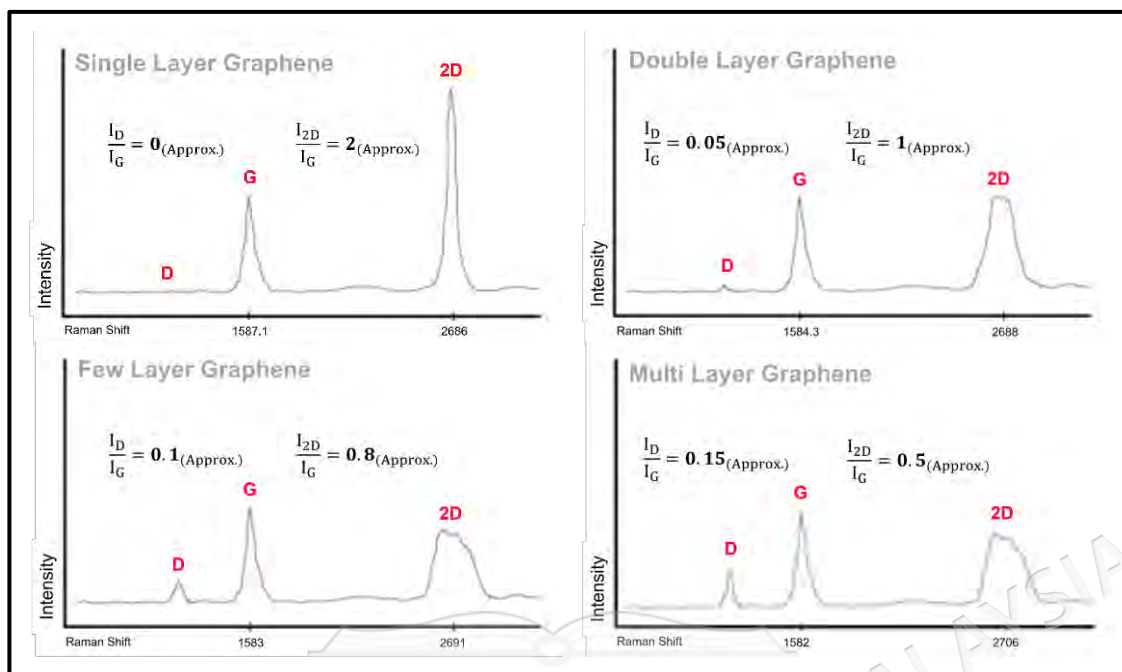


Figure 3.7 Classification of graphene layer.

Source: InstaNANO <https://instanano.com/all/characterization/raman/graphene-layers/> (accessed February 18th, 2021).

3.7.2 Morphological and elemental analysis

The morphology of the Ni-based substrates, graphene/Ni-foam, and ZnO/graphene/Ni-foam photoelectrode was characterized using a FESEM at i-CRIM Centralized Laboratory, UKM. This technique utilizes an electron beam to produce high resolution images of samples, down to the nanometer scale. The accelerating voltage typically ranges from 0.50 to 30 kV. To prevent charging effects during the FESEM imaging, the samples are coated with a thin layer of Pt. The elemental distribution across the samples surface is visualized by Energy Dispersive X-ray (EDX) mapping. To obtain cross-sectional images, the samples were mechanically cleaved with a blade and mounted onto a sample holder oriented at a 90° angle. All the elements in the sample emit X-rays with their own particular energies. In this study, the color of each element is standardized to yellow for zinc, green for oxygen, red for carbon and cyan for Ni. To examine ZnO/graphene/Ni-foam post-characterization morphological stability, FESEM characterization was performed directly on the sample after 3 hours stability testing, without undergoing any additional surface treatment.

3.7.3 Structural and crystallinity analysis

The crystalline structure of the photoelectrode was determined using XRD at Faculty of Science and Technology (FST), UKM. This technique relies on the dual wave-particle nature of X-rays to probe the atomic arrangement within crystalline materials. The photoelectrode was put directly on the sample holder without any treatment. The XRD measurements were performed using a Cu K α radiation source ($\lambda = 1.54184 \text{ \AA}$) with a 2θ scan range of $20 - 80^\circ$ at room temperature. The XRD diffractograms were further analyzed using X'pert HighScore Plus software to identify the crystal phases.

3.7.4 Light absorption and band gap analysis

The light absorption properties of the photoelectrode will be investigated using UV-Vis spectroscopy at i-CRIM Centralized Laboratory, UKM. This technique measures the absorbance of light across the UV and visible regions of the spectrum, specifically within the wavelength range of $200 - 1200 \text{ nm}$. The UV wavelengths range from $100 - 400 \text{ nm}$, while the visible range extends from $400 - 800 \text{ nm}$. By analyzing the spectrum, the E_g of the photoelectrode can be estimated by converting the data to Tauc plot using Equation (3.1) (Gulab et al. 2022).

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad \dots (3.1)$$

where α is the optical absorption coefficient, $h\nu$ is the incidence photon energy, A is the proportionality constant, and ν is the frequency. The E_g is determined by extrapolating the linear section of the $h\nu - \frac{(\alpha h\nu)^2}{A}$ to $\frac{(\alpha h\nu)^2}{A} = 0$ (Wang et al. 2017).

3.7.5 Elemental composition analysis

The information on the elemental composition, oxidation states, and types of chemical bonding in the photoelectrode is determined using XPS at i-CRIM Centralized Laboratory, UKM. This technique works by irradiating atoms of the surface of the photoelectrode with X-ray photons, causing the ejection of electrons. The X-ray source use is $\text{AlK}\alpha$ (1486.60 eV) and XPS can only detects the surface elemental composition with depth profile close to 10 nm (Krishna & Philip 2022). The analysis was performed by running a survey scan at E_b of 0 – 1200 eV, followed by high resolution scans at Zn 2p, O 1s, C 1s and Ni 2p regions. The results were analyzed using CASA XPS software. All E_b were calibrated to the C 1s peak at 284.40 eV.

3.8 PEC CHARACTERIZATION

Electrochemical characterization is a method to study how chemical reactions happen in the presence of an electric current. There are four techniques involved: (i) LSV, (ii) EIS, (iii) Mott-Schottky, and (iv) CA. These techniques can be used to determine photoactivity, photocurrent onset potential, the maximum photocurrent (mA/cm^2 vs RHE), the Applied Bias Photon-to-current Efficiency (ABPE; %), the charge transfer efficiency (Ω), the carrier density value ($1/\text{cm}^3$), and the stability ($\text{mA}/\text{cm}^2/\text{s}$) of the photoelectrode. All characterizations were performed at room temperature.

The experimental set up for PEC measurements consists of a PEC cell, an Xe lamp with a filter as the light source, and a potentiostat (Figure 3.8). A three-electrode system is employed within the PEC cell, containing the WE (photoelectrode with an active area of 1.50 cm^2), the CE (Pt coil), and the RE (Ag/AgCl saturated with 3 M KCl). Then, the cell is filled with 30 mL of 0.50 M Na_2SO_3 electrolyte (pH = 10). Before each measurement, the electrolyte is purged with nitrogen gas for 30 minutes to remove dissolved O_2 gas, as described by Butler et al. (1994).

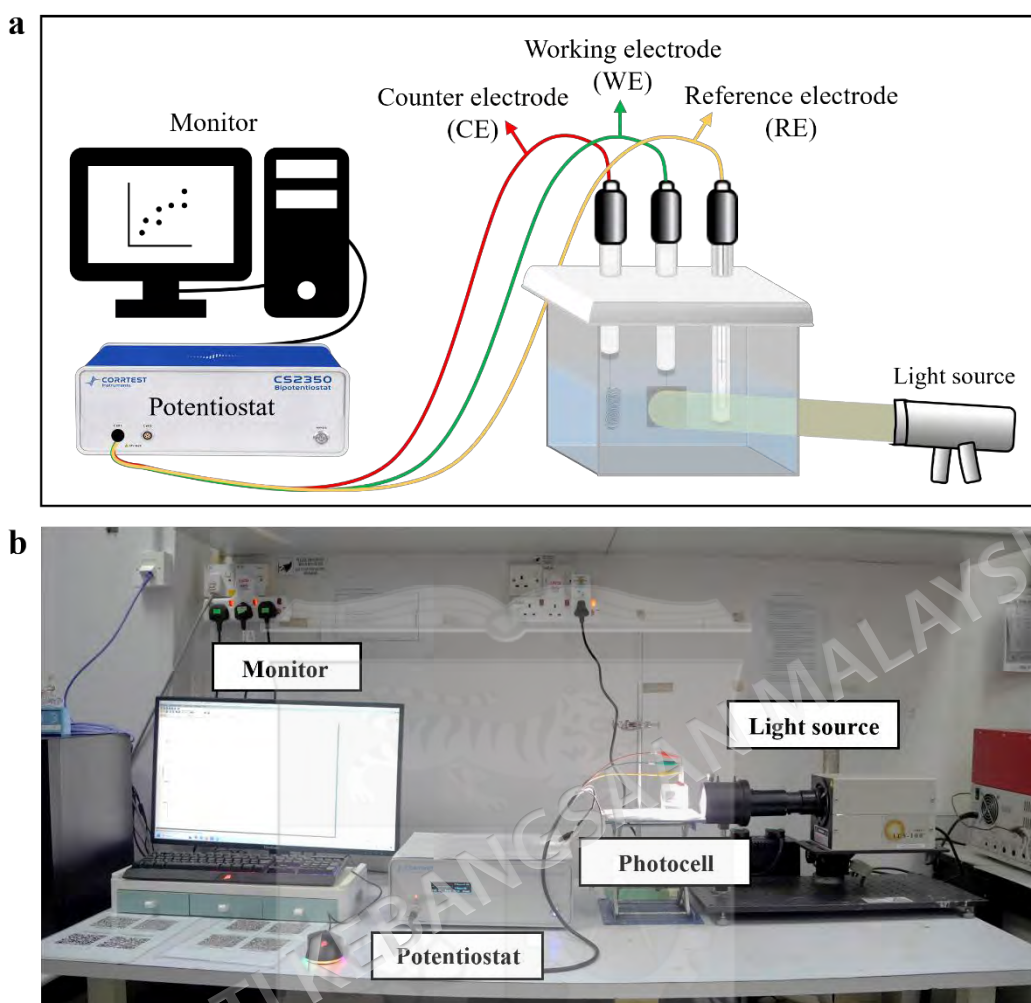


Figure 3.8 (a) Schematic illustration and (b) the actual experimental setup for PEC measurements.

3.8.1 Photocurrent and stability analysis

The photocurrent density is the most important and common parameter for evaluating the performance of the photoelectrode. LSV is a common technique to characterize the response of the photoelectrode by measuring photocurrent density versus applied potential (Sahu et al. 2024). Typically, it is conducted under both light and dark conditions. The light source simulates one sun illumination (100 mW/cm^2) with AM 1.5G filter, while the dark condition excludes any external light. The measurements are performed from 0 to 1.00 V vs Ag/AgCl at a scan rate of 50 mV/s. The difference in current density measured under light and dark conditions represents the photocurrent density generated by the photoelectrode. Data will be collected from three replicate

samples; the average values will be reported and converted to Reversible Hydrogen Electrode (RHE) values using Equation (3.2):

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + (0.059 \times \text{pH}) + 0.1976 \quad \dots (3.2)$$

Besides, the ABPE was measured from the LSV measurements to evaluate the photoelectrode's ability to convert incident photons into H_2 under operational conditions (Rosman et al. 2025). The ABPE represents the overall efficiency of PEC energy conversion and is calculated using the following equation:

$$ABPE (\%) = \frac{J_{\text{ph}} (V_{\text{rev}}^0 - V_{\text{app}})}{P_{\text{light}}} \times 100\% \quad \dots (3.3)$$

where J_{ph} is the photocurrent density (mA/cm^2), V_{rev}^0 is the standard reversible potential for water splitting (1.23 V), V_{app} is the applied potential, and P_{light} is the incident light intensity ($100 \text{ mW}/\text{cm}^2$). For practical applications, the photoelectrode must also exhibit stable performance over time. To evaluate this, the stability of the photoelectrode was evaluated using CA under two testing: (i) chopped illumination with 20 seconds intervals for light and dark for 10 minutes, and (ii) stability under continuous illumination for three hours. Both measurements were conducted at a constant applied potential of 0.40 V vs Ag/AgCl (onset potential). These analyses provide quantitative insights into the photocurrent stability, which serves as a fundamental indicator of the photoelectrode's effectiveness.

3.8.2 Resistance analysis

The photoelectrode's performance is primarily determined by its ability to separate and transfer photogenerated charge carriers. EIS offers a valuable technique to analyze the various resistance components within the photoelectrode from the Nyquist plot (Magar et al. 2021). To understand the information on charge transfer resistance, series resistance, and other factors occurring at the photoelectrode–electrolyte interface, EIS is measured in dark condition in the range of 100 kHz to 1 kHz with amplitude 0.10 V at 0.40 V vs Ag/AgCl (onset potential). Then, it will be fitted with the raw data using

Corrtest Analysis software and equivalent circuit modeling is determined, where the Randles model with a constant phase element (CPE-Rp) was used. This model consists of ohmic resistance of the electrolyte solution (R_s), charge transfer resistance across the substrates and the photoelectrode (R_1), charge transfer resistance across the photoelectrode and the electrolyte (R_2) and the corresponding dispersive resistance factors (CPE1 and CPE2) of R_1 and R_2 , respectively. These measure resistances are calculated for understanding the overall efficiency of PEC activities.

3.8.3 Mott-Schottky

Understanding the semiconducting properties of a photoelectrode is essential for optimizing the charge transfer characteristics, which directly impacts PEC performance. Mott-Schottky analysis provides a method to determine the conductivity type and carrier density by measuring the interfacial capacitance as a function of applied potential (Hankin et al. 2019; Sivula 2021). The measurements were performed across a potential range of -1.00 to +1.00 V vs Ag/AgCl, utilizing a 0.10 V amplitude at a frequency of 1 kHz. The slope of the resulting Mott-Schottky plot reveals the conductivity type: p-type for positive slope while n-type for negative slope of the photoelectrode (Adris et al. 2024; Sivula 2021).

Other than that, the carrier density (p-type for electron acceptor; N_a and n-type for electron donor; N_d) is calculated from the slope of the Mott-Schottky plot using the following equations (Sivula 2021; Windisch & Exarhos 2000):

For p-type semiconductors:

$$N_a = \frac{-2}{e\epsilon\epsilon_0 A^2 (\text{slope})} \quad \dots (3.4)$$

For n-type semiconductors:

$$N_d = \frac{2}{e\epsilon\epsilon_0 A^2 (\text{slope})} \quad \dots (3.5)$$

where e is the electron charge (1.6022×10^{-19} eV), ϵ is the dielectric constant of NiO (11.9) (Rao & Smakula 1965) was used (as the Ni-foam substrate served as the control sample), ϵ_0 is the permittivity of free space (8.8542×10^{-14} F/cm), N_a is the electron acceptor, N_d is the electron donor, and A is the area of the photoelectrode.

3.8.4 Hydrogen production

The hydrogen (H_2) production was measured using GC at Low Dimensional Research Center, Universiti Malaya. The GC used was equipped with a Thermal Conductivity Detector (TCD) gas chromatograph and Ar gas is used as the carrier gas. The experimental setup is almost the same as mentioned in Section 3.8, with a different cell, known as an H-cell (Figure 3.9). This cell has two parts: one part for the WE and the other part for the CE and RE. The cell is filled with approximately 320 mL of 0.50 M Na_2SO_3 electrolyte (pH = 10). During the H_2 measurements, the generated gases were transferred to a test tube and pumped into sample loop using a peristaltic pump. After that, the gas was measured using GC under online monitoring mode. The gas was separated using MS-5A and HayeSep Q columns.

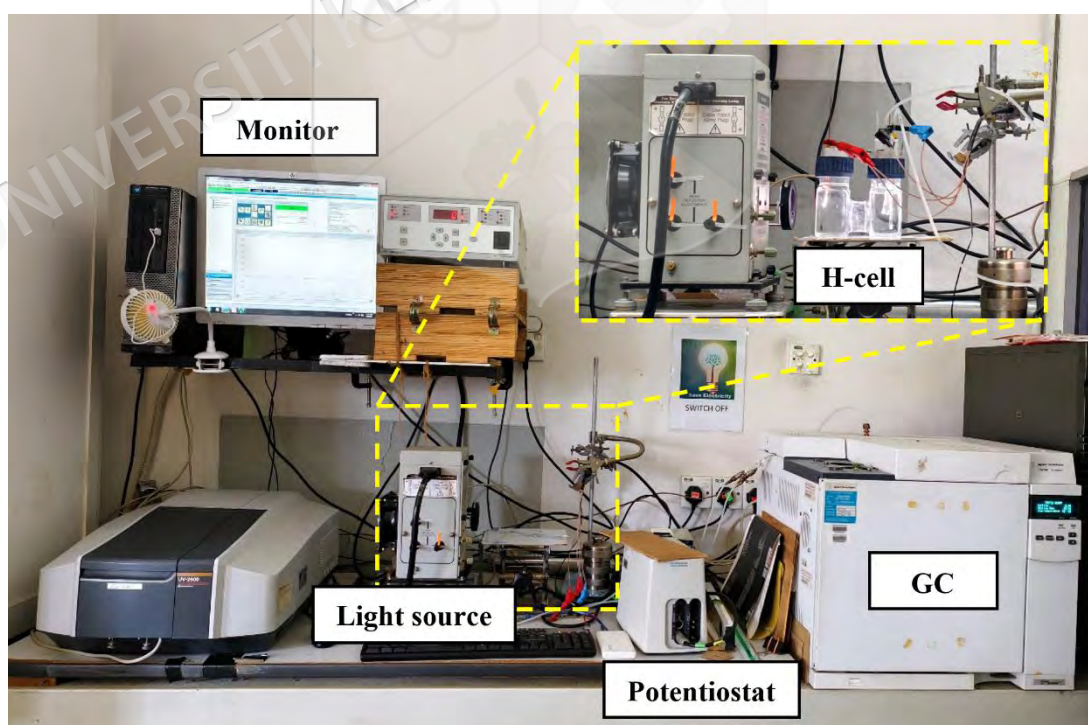


Figure 3.9 Experimental setup for GC analysis (inset: H-cell configuration).

The amount of H₂ produced was determined by correlating the GC data with the calibration curve. Subsequently, the Faraday Efficiency (FE) was calculated to evaluate the effectiveness of generated electron for H₂ production, as expressed in Equation (3.6) (Hamdani & Bhaskarwar 2021; Mosa et al. 2015):

$$FE (\%) = \frac{\eta_{\text{experiment}}}{\eta_{\text{theoretical}}} \times 100\% \quad \dots (3.6)$$

$$\eta_{\text{theoretical}} = \frac{Q}{2F}, \text{ where } Q = I \times t \quad \dots (3.7)$$

where $\eta_{\text{experiment}}$ is the molar flowrate obtained from experimental measurements (mol/s), $\eta_{\text{theoretical}}$ is the theoretical molar flowrate (mol/s), Q is the total charge (C), F is the Faraday constant (96,485 C/mol), I is current (A), and t is reaction time (second). After that, the STH efficiency was calculated to evaluate the material capability to generate H₂ under unassisted conditions using Equation (3.8):

$$STH = \left[\frac{(r_{\text{H}_2})(\Delta G)}{(P_{\text{in}})(A)} \right] \times 100\% \quad \dots (3.8)$$

where r_{H_2} is the H₂ production rate (mmol/second), ΔG is Gibbs free energy for water splitting (237 kJ/mol at 25 °C), P_{in} is the light intensity (mW/cm²), and A is the illuminated area (cm²). Initially, the STH efficiency is determined by assuming a FE of 100%. To measure the actual STH efficiency based on experimental results, the measured FE is calculated using Equation (3.9):

$$STH_{\text{actual}} = STH_{100\%} \times FE \quad \dots (3.9)$$

3.9 DENSITY FUNCTIONAL THEORY (DFT)

In this study, Density Functional Theory (DFT) calculations were performed using the STATE-Senri package, developed by Morikawa et al. (2001) at The University of Osaka, Japan, to model the ZnO/graphene/Ni system. The Generalized Gradient Approximation (GGA) with the Perdew-Burke-Enzerhof (PBE) exchange-correlation functional is utilized to tackle all electronic energy of exchange correlation. The plane

wave basis sets were employed with energy cutoffs of 36 Ry for wave functions and 400 Ry for charge density. Besides, the k -point used is $4 \times 4 \times 1$. To describe the long-range interaction (vdW), the DFT-D2 exchange-correlation functional was used (Xu et al. 2013).

At the beginning, the isolated systems (ZnO, graphene, and Ni) were optimized individually until stable structures were developed. Then, these optimized structures were combined to construct the ZnO/graphene/Ni system. It should be noted that this ZnO/graphene/Ni structure in DFT model serves as an idealized representation of the actual experimental interface. To ensure the stability and efficiency of this combined system, the lattice mismatch between ZnO-graphene and graphene-Ni should be smaller than 3%. For this reason, the Ni (111) surface was employed as the substrate surface due to its near-perfect lattice mismatch with graphene to preserve the electronic and structural integrity of the ZnO/graphene/Ni system. Since Ni is hard and ductile, graphene is flexible, and ZnO is rigid material, the lattice constant of graphene and Ni was adjusted to the ZnO. Therefore, the supercell size of the system was carefully chosen, where the lattice constant of graphene and Ni was adjusted to the ZnO. In this study, two different surfaces of polar ZnO were chosen: Zn-terminated (0001) (Zn atom at the top layer) and O-terminated (000 $\bar{1}$) (O atom at the top layer), with equal amount of Zn and O on the surface (Xu et al. 2013). While for graphene-Ni, Bridge-top and Top-fcc were determined to be the most stable interfaces (Christian et al. 2017). Thus, these interfaces were considered.

Next, the dangling bond at the bottom layer of ZnO surfaces will be saturated with pseudohydrogen (H) to reduce the internal electric field accelerate convergence and mimic the bulk property of bulk ZnO (Xu et al. 2013). Charges of 0.5e and 1.5e H were used for Zn-terminated (O atom at the bottom layer) and O-terminated (Zn atom at the bottom layer) ZnO, respectively. Each model is made up of 3×3 -unit cells of 3 bilayers of ZnO (54 atoms with 27 Zn and 27 atoms), a 4×4 repetition of graphene (32 C atoms), and 3 layers of Ni (48 Ni atoms). The spin polarization was included for Ni. The supercells are constructed in a slab configuration with a 37.04 Å vacuum layer to reduce any interactions between periodic images. All parameters are tabulated in Table 3.3.

Table 3.3 Basic parameters setting for geometry optimization of ZnO/graphene/Ni.

Parameters		Computational Details
Code		STATE-Senri
Functional		GGAPBE-D2
<i>k</i> -point		4 x 4 x 1
Energy cutoff		Wave function: 36 Ry Charge density: 400 Ry
Vacuum layer		37.04 Å
Unit cell (number of atoms)	3 x 3 of 3 bilayers of ZnO	(54)
	4 x 4 repetition of graphene	(32)
	3 layers of Ni	(48)
Surface	Zn-terminated ZnO (0001)	Fixed 3 bottom layers (Zn, O, H)
	O-terminated ZnO (000 $\bar{1}$)	
Interface	Bridge-top graphene–Ni	Fixed topmost Ni layer
	Top-fcc graphene–Ni	

Geometry optimization was performed by fully relaxing all atoms. However, the bottom three layers of Zn, O, H (representing bulk ZnO), and the topmost Ni layer were fixed at its position. This was done to allow for realistic surface reconstruction. To accurately investigate the interfacial interactions of the three materials, the interlayer distance between the topmost Ni layer and the first layer of ZnO was systematically varied to identify the most optimized configuration. Besides, the optimization process will be repeated until the forces on all atoms were reduced to less than 0.05 eV/Å, a standard convergence criterion in DFT calculations for accurate adsorbate-surface interactions (Al Fauzan et al. 2025).

The binding energies (E_b), the binding energies per carbon atom ($E_{b/n}$), and the interaction energies (E_{int}) of the system will be calculated using following equation (Geng et al. 2013):

$$E_b = E_{\text{ZnO/graphene/Ni}} - E_{\text{ZnO}} - E_{\text{graphene}} - E_{\text{Ni}} \quad \dots (3.10)$$

$$E_{b/n} = E_b/n \quad \dots (3.11)$$

$$E_{int} = E_{\text{ZnO/graphene/Ni}} - (E_{\text{ZnO/graphene}} + E_{\text{graphene/Ni}}) \quad \dots (3.12)$$

where the $E_{\text{ZnO/graphene/Ni}}$ represent the total energy of the combined ZnO/graphene/Ni system, while E_{ZnO} , E_{graphene} , and E_{Ni} are the total energies of the isolated ZnO,

graphene, and Ni, respectively, and n is the number of carbon atoms. A negative E_b and $E_{b/n}$ indicates a stable adsorption structure (Geng et al. 2013; Zhang et al. 2014). While for vdW interaction, it will be calculated using following equation:

$$vdW = vdW_{ZnO/graphene/Ni} - vdW_{ZnO} - vdW_{graphene} - vdW_{Ni} \quad \dots (3.13)$$

where the $vdW_{ZnO/graphene/Ni}$ represents the vdW correction of the combined ZnO/graphene/Ni system, while vdW_{ZnO} , $vdW_{graphene}$, and vdW_{Ni} are the vdW correction of the isolated ZnO, graphene, and Ni, respectively. The difference between E_b and vdW was analyzed to determine the nature and strength of the interfacial interactions, thereby distinguishing whether the system is governed by weak vdW forces (physisorption) or stronger chemical interactions (chemisorption). All structural models and electronic configurations were visualized and analyzed using VESTA software and Python scripts.

3.10 CHARGE TRANSFER MECHANISM

3.10.1 Experimental method

To systematically investigate the charge transfer mechanism of ZnO/graphene/Ni-foam, a combination of UV-Vis, LSV, EIS, and Mott-Schottky was employed. While these techniques characterize the optical and PEC properties, the underlying charge transfer mechanism is usually estimated by the energy level alignment of the semiconductors. The positions of the CB and the VB of the photoelectrode were determined using the Mulliken electronegativity theory. The electronegativity (X) of ZnO need to be calculated first (Barpuzary et al. 2015). The X values for each atom can be derived from Equation (3.14):

$$X_{Zn,O} = \frac{1}{2} (IP_{Zn,O} + EA_{Zn,O}) \quad \dots (3.14)$$

where IP is the ionization potential and EA is the electron affinity of the Zn and O. Then, the overall X of ZnO can be calculated using Equation (3.15):

$$X_{\text{Zn,O}} = (X_{\text{Zn}}^a X_{\text{O}}^b)^{\frac{1}{(a+b)}} \quad \dots (3.15)$$

where a and b are the number of atoms of Zn and O in ZnO, respectively. Based on these values, the position of the CB and VB can be measured using the following equations (Fareza et al. 2022):

$$\text{CB} = X + E_0 - \frac{E_g}{2} \quad \dots (3.16)$$

$$\text{CB} = \text{VB} - E_g \quad \dots (3.17)$$

where E_0 is the energy of a free electron on the hydrogen scale (-4.5 eV) and E_g is the band gap energy of the ZnO.

3.10.2 Computational method

The information of the electronic band structure and the position of the VB and CB of ZnO/graphene/Ni system can be determined once the stable structure was developed. Specifically, the Layer Density of States (LDOS) analysis was employed to provide a detailed picture of the electronic properties across the interface of the photoelectrode. By determining the position of the VB and CB from the LDOS, the energy level alignment of the photoelectrode can be estimated. This is important for predicting the PEC performance of the ZnO/graphene/Ni system.

To understand on how electron is transferred between the materials, the charge density different (CDD) calculations were performed using Equation (3.18):

$$\text{CDD} = \rho_{\text{ZnO/graphene/Ni}} - \rho_{\text{ZnO}} - \rho_{\text{graphene}} - \rho_{\text{Ni}} \quad \dots (3.18)$$

where $\rho_{\text{ZnO/graphene/Ni}}$ represents the charge density of the combined ZnO/graphene/Ni system, while ρ_{ZnO} , ρ_{graphene} , and ρ_{Ni} are the charge density of the isolated ZnO, graphene, and Ni, respectively. By visualizing the CDD, the charge transfer mechanism can be observed.

3.11 CONCLUSION

Overall, this chapter presents a comprehensive overview of the experimental and theoretical methodologies used to achieve the objectives of this study. Initial screening was carried out to identify the most ideal Ni-based substrate for the growth of ZnO/graphene. After substrate selection, graphene was synthesized using the CVD method by tuning the annealing time, flow rate of CH₄, and growth time. The effects of these parameters were evaluated using physicochemical characterizations like FESEM, EDX, Raman, XRD, UV-Vis and XPS. Finally, the optimized graphene on Ni substrate was successfully synthesized using the CVD method.

After that, ZnO was deposited onto the graphene/Ni substrate using hydrothermal method by controlling the reaction temperature. FESEM, EDX, and XRD analysis were conducted to determine the optimal synthesis condition. Then, the final ZnO/graphene/Ni photoelectrode was further characterized using UV-Vis, XPS as well as the PEC characterization like LSV, ABPE, EIS, Mott-Schottky, CA (chopping and stability) and H₂ production, with comparisons made against control sample (Ni-foam).

Subsequently, DFT calculations were performed to investigate the interfacial interaction and validate the charge transfer mechanism within the ZnO/graphene/Ni system. In the end of this study, the charge transfer mechanism and PEC performance of the ZnO/graphene/Ni photoelectrode were elucidated through a combine experimental and theoretical approach.

CHAPTER IV

RESULT AND DISCUSSION

4.1 INTRODUCTION

This chapter presented the findings and interpretations derived from both experimental and theoretical studies, emphasizing the structure and performance relationship, hydrogen (H₂) production rate, and their roles in enhancing charge transfer mechanism. This chapter is organized into seven main sections: (1) the selection of the suitable substrate for PEC applications, (2) the growth of graphene on the Nickel (Ni) substrate using CVD method, (3) the growth of ZnO on graphene/Ni using hydrothermal method, (4) the PEC characterization of ZnO/graphene/Ni photoanode, (5) the evaluation of H₂ production performance, (6) the investigation of interfacial interactions within the ZnO/graphene/Ni using Density Functional Theory (DFT), and (7) the elucidation of the charge transfer mechanism based on experimental and DFT results.

4.2 MORPHOLOGICAL AND ELECTROCHEMICAL CHARACTERIZATION OF NICKEL SUBSTRATES

Nickel (Ni) was selected as the substrate material for graphene growth due to its lattice compatibility, excellent electrical conductivity, mechanical robustness, and corrosion resistance in alkaline media, as mentioned in Chapter II. This study utilized two types of Ni substrates: Ni-foil and Ni-foam. While the primary focus of this research is on nanostructure growth, a preliminary selection of the substrate was essential to identify the most suitable substrate for achieving high surface area and superior charge transfer. The selection was based on their morphological and electrochemical characteristics, as determined by FESEM and EIS for impedance analysis.

4.2.1 Morphological

Although Ni-based substrates share similar intrinsic properties, their surface morphologies are significantly different. Figure 4.1 presents the FESEM images comparing the morphological structure of Ni-foil and Ni-foam. As shown in Figure 4.1 (a), the Ni-foil exhibits a typical planar and dense morphology and minimal porosity. The observed surface smoothness and minor defects are attributed to the mechanical rolling process during manufacturing, resulting in a low surface area (Deokar et al. 2020). Meanwhile, Figure 4.1 (b) shows the morphology of the Ni-foam which exhibits a fully interconnected, sponge-like architecture with large open pores. Consequently, the Ni-foam is expected to have higher number of active sites and higher electrolyte accessibility compared to Ni-foil. This morphological advantage is verified by the electrochemical performance presented in the following section.

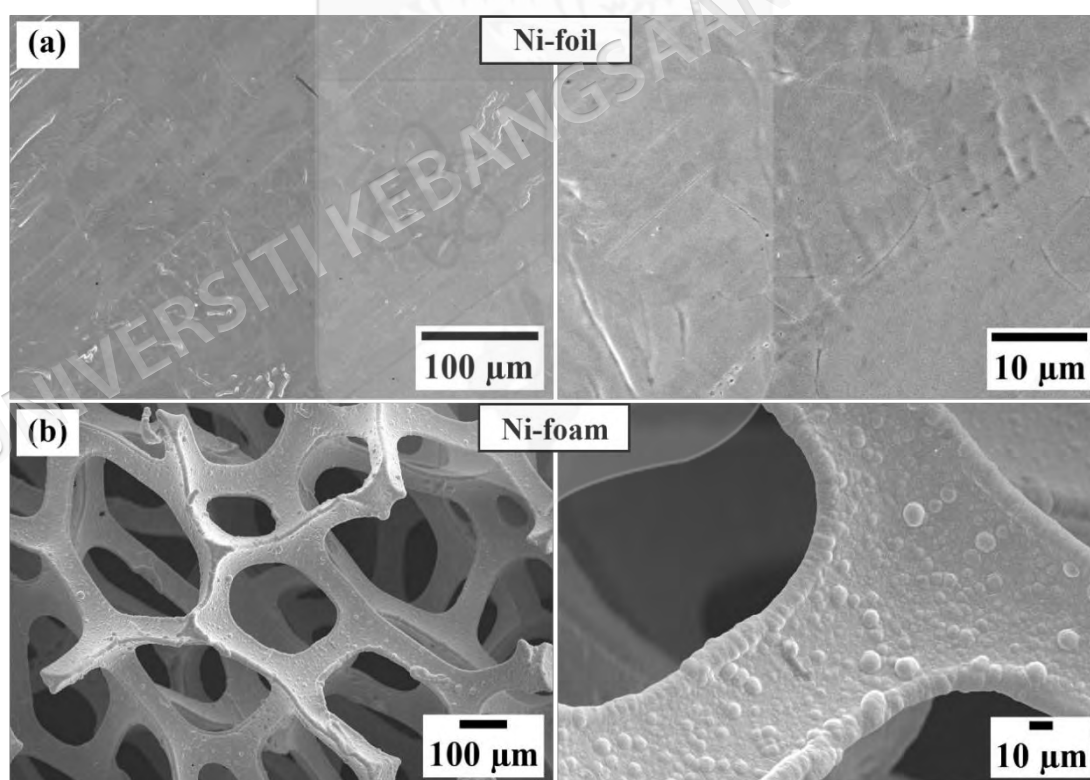


Figure 4.1 FESEM images of (a) Ni-foil and (b) Ni-foam at low (100x) and high (500x) magnifications.

4.2.2 Electrochemical Impedance Analysis

To further confirm the charge transfer behavior of both substrates, EIS was conducted. To quantify the impedance parameters, the experimental data were fitted to an equivalent circuit, consisting of a solution resistance (R_s) in series with a parallel combination of a constant phase element (CPE) and charge transfer resistance at the electrode-electrolyte interface (R_1), which also observed by Grdeń et al. (2012). Figure 4.2 shows the Nyquist plots for both substrates.

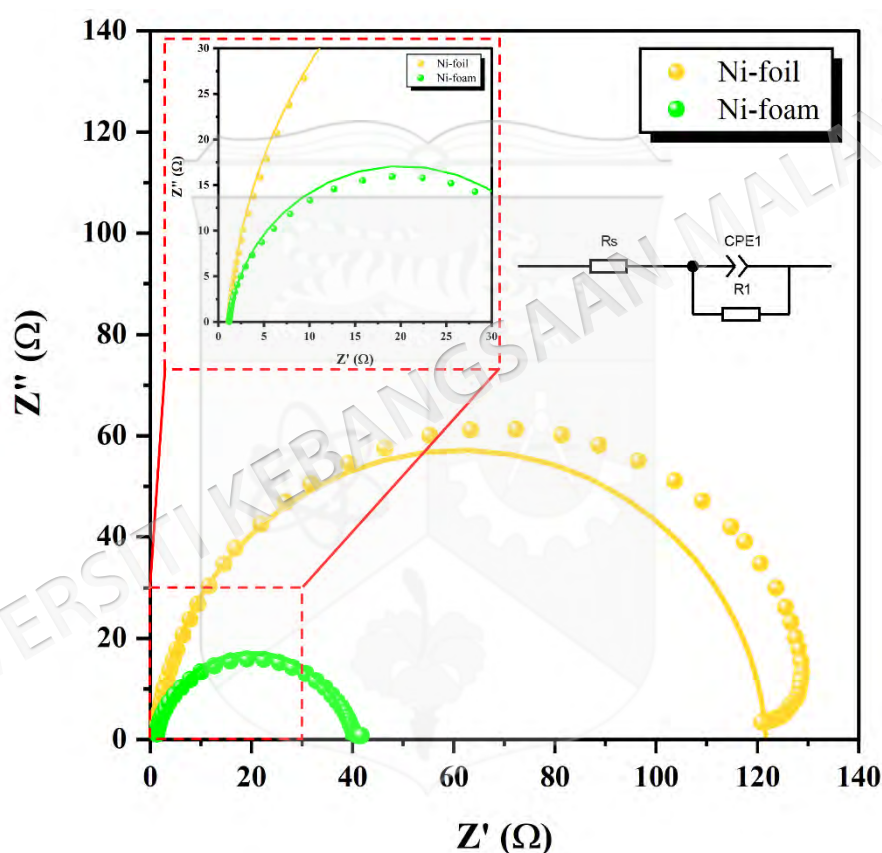


Figure 4.2 Nyquist plots derived from EIS measurements for Ni-foil and Ni-foam (the solid lines represent the fitting results) with the equivalent electrical circuit used to fit the experimental data.

A CPE was utilized in the equivalent circuit models for both Ni-foil and Ni-foam substrates to account for frequency dispersion. While Ni-foil is macroscopically flat (from FESEM analysis in Figure 4.1 (a)), its macroscopic surface roughness, grain boundaries, and the presence of native oxide layers result in non-ideal capacitive behavior. For the Ni-foam, this effect is further amplified by its complex 3D porous

structure. Table 4.1 summarizes the R_s , CPE, and R_1 values for both substrates. The fitting results reveal that Ni-foam displays a significantly lower R_1 value (37.90 Ω) compared to the Ni-foil (120.47 Ω), observed by its smaller semicircle radius. This confirms that the 3D interconnected structure of the Ni-foam not only provides a high surface area but also facilitates faster electron transfer and superior interfacial contact with the electrolyte (Anuar et al. 2024). Thus, the overall resistance losses are reduced compared to Ni-foil.

Table 4.1 Summary of electrochemical impedance parameters derived from equivalent circuit fitting for Ni-foil and Ni-foam.

Sample	R_s (Ω)	CPE	R_1 (Ω)
Ni-foil	1.20	0.97	120.47
Ni-foam	1.20	0.93	37.90

The preliminary analysis clearly demonstrates the differences between Ni-foil and Ni-foam substrates for PEC applications. FESEM images reveal that the Ni-foam exhibits a 3D interconnected porous structure, offering a significantly higher surface area compared to the 2D planar surface of Ni-foil. Furthermore, EIS analysis indicates that the Ni-foam exhibits a lower R_{ct} compared to the Ni-foil. This improvement is attributed by to the higher surface area provided by the porous architecture of Ni-foam, which is advantageous for electrolyte accessibility and promotes more efficient gas bubble release. Therefore, based on its favourable morphology and excellent electrochemical performance, Ni-foam was selected as the ideal substrate for the subsequent synthesis of ZnO/graphene.

4.3 INFLUENCE OF CVD GROWTH PARAMETERS ON AS GROWN GRAPHENE STRUCTURE

Based on the findings of the preliminary study, Ni-foam was chosen as a substrate for graphene growth. To achieve a uniform and high-quality graphene layer, the synthesis parameters were systematically controlled throughout the four main step of the CVD temperature profile, as described by Muñoz & Gómez-Aleixandre (2013). First, the heating process increased the temperature from room temperature to 1000 °C. This pre-process treatment provided the necessary thermal energy for the reaction. Second, the annealing process, to maintain the temperature under a controlled gas atmosphere. This

step is essential to make sure the Ni-foam surface is clean from impurities (such as oxides) and to modify the surface morphology by improving crystalline orientation and increasing grain size.

Next, the growth process. Here, CH_4 was supplied as a carbon source. The CH_4 molecules chemisorbed onto the Ni-foam surface and dissociated through dehydrogenation. Then, the dissociated carbon atoms diffused into the Ni lattice. Finally, the cooling process. The temperature is reduced back to room temperature. This step drives the segregation of carbon atoms to the surface of the Ni-foam, leading to the nucleation and the formation of graphene layers while maintaining an inert atmosphere to prevent oxidation (Ago et al. 2015). The CVD temperature profile of graphene growth on Ni-foam is presented in Section 3.5.2. Through this steps, graphene/Ni-foam was successfully synthesized using CVD method, as illustrated in Figure 4.3. Ni-foam acts as a control sample to confirm the improvement of the synthesized samples.

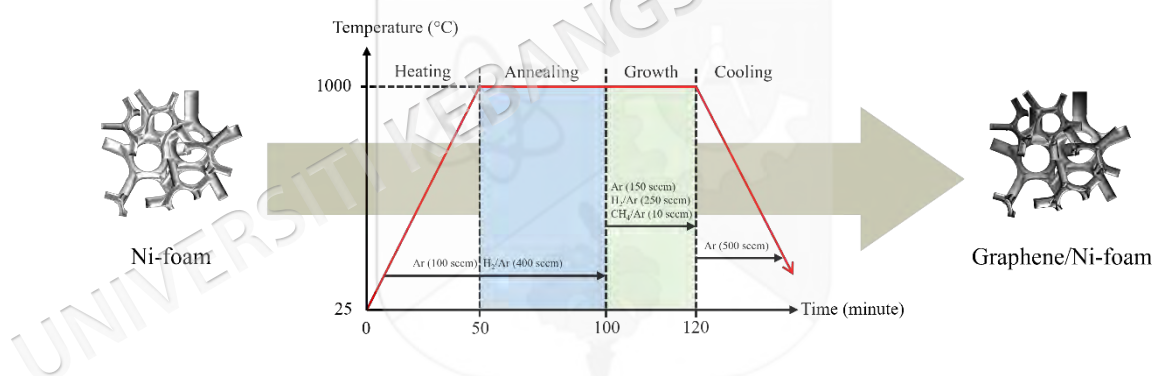


Figure 4.3 Schematic illustration of graphene growth on Ni-foam via CVD.

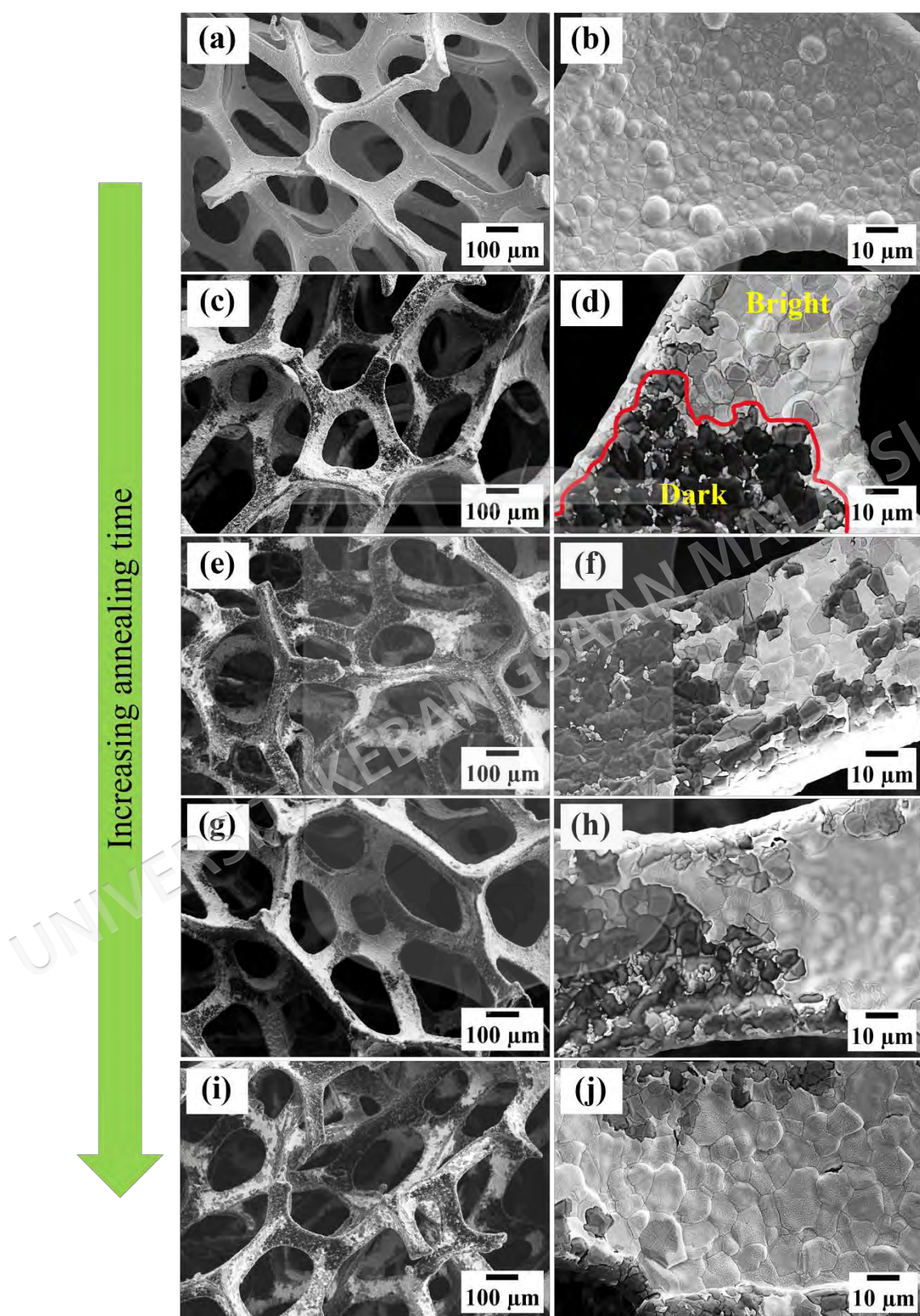
4.3.1 Annealing time

For graphene growth via CVD method, annealing time plays an important role. As stated previously, the annealing process is critical for removing surface oxides and modifying the Ni morphology by improving crystalline orientation and increasing grain size (Muñoz & Gómez-Aleixandre 2013; Saeed et al. 2020). Here, annealing time was varied from 0, 20, 30, 40, 50, and 60 minutes. The CH_4 flow rate and growth time were fixed at 20 sccm and 30 minutes, respectively. Figure 4.4 displays FESEM images of the synthesized samples. As annealing time increases, two colour contrast: dark and bright, are observed. The bright areas are expected to represent the Ni-foam, while the

darker regions are graphene, because based on the principle of FESEM, higher atomic number of Ni (28) compared to carbon (6) leads to stronger electron backscattering (Ali et al. 2023). This will be confirmed by subsequent EDX mapping analysis.

Interestingly, graphene still formed on the unannealed Ni-foam sample (Figure 4.4 (c, d)). This is because the high temperature exposure during heating step is already sufficient to drive carbon dissolution into the Ni bulk (Ago et al. 2015; Saeed et al. 2020). However, the presence of nickel oxide (NiO) and other impurities are expected due to exposure to high temperatures during the CVD process, which will be further confirmed by XRD analysis. Next, the coverage area of graphene on the Ni-foam improved with increased annealing time, reaching its maximum at 50 minutes (Figure 4.4 (e – l)). The resulting graphene displays some ripples and wrinkles. These features are observed due to the different thermal expansion coefficients between Ni and graphene, and might be due to the lattice mismatch between these two materials (Bello et al. 2013; Geng et al. 2013).

As the annealing time is extended to 60 minutes, a reduction in coverage area of graphene is observed (Figure 4.4 (m, n)). This behaviour is attributed to the instability in the kinetic conditions required for graphene growth. While the carbon active species concentration increases until it reaches a critical supersaturation level, the decrease in graphene coverage is driven by the prolonged interaction with the H₂ atmosphere. Here, the high diffusivity and solubility of H within the Ni-foam substrate play a key role. At longer annealing times, H atoms that were previously absorbed into the Ni surface migrate back to the surface, where H-H recombination and desorption occur. While this process continuously modifies the surface of Ni to generate additional active sites for CH_x dissociative chemisorption, high thermal energy simultaneously enhances the H₂ etching reaction (Chaitoglou & Bertran 2017; Jin et al. 2014; Saeed et al. 2020). Consequently, the relationship between graphene nucleation density, lateral growth rate and surface coverage area, leading to non-uniform growth and a reduction in overall graphene coverage.



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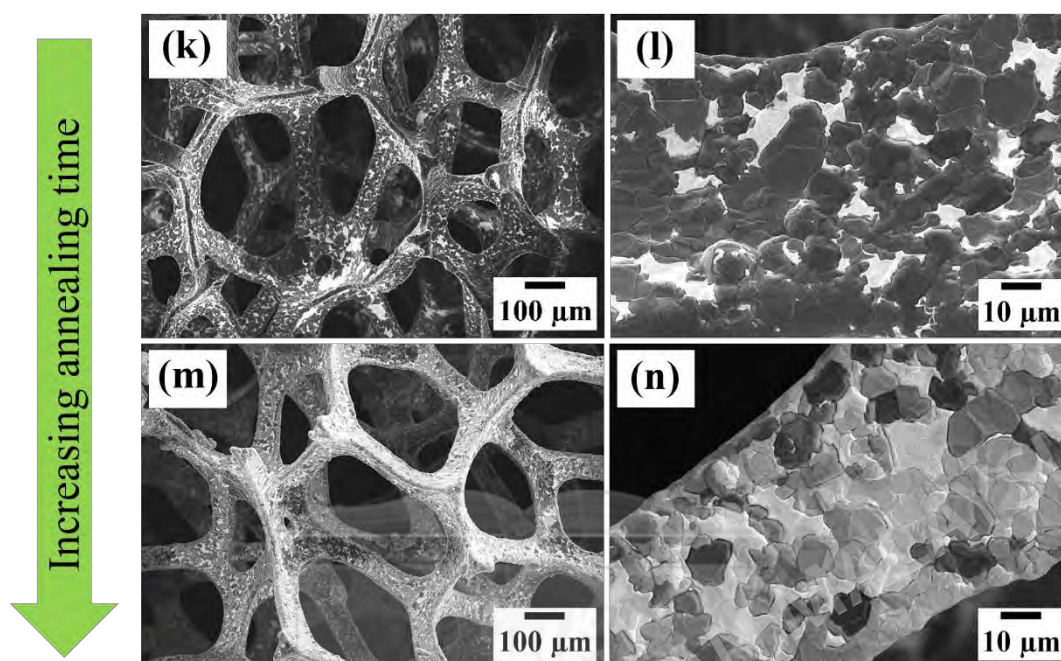


Figure 4.4 FESEM images at low (100x) and high (1,000x) magnifications of graphene on Ni-foam with different annealing times (a, b) Pure Ni-foam, (c, d) 0, (e, f) 20, (g, h) 30, (i, j) 40, (k, l) 50, and (m, n) 60 minutes (CH_4 flow rate: 20 sccm, growth time: 30 minute).

As confirmed by the EDX mapping analysis in Figure 4.5, the different colour contrast observed in the FESEM images is consistent with the elemental distribution, where the bright regions correspond to Ni-foam substrate, and the dark regions correspond to graphene. This finding confirms that successful growth of graphene on Ni-foam surface. However, there are some areas of the Ni-foam remains uncoated with graphene. Jin et al. (2014) investigated the role of H_2 during the annealing step of CVD graphene growth and the findings revealed that the non-uniform coverage of graphene on substrate is likely due to the limitations in the growth kinetics, due to the insufficient H_2 source during the annealing process. An insufficient H_2 sources during annealing results in smaller grain sizes, which hinders the growth process.

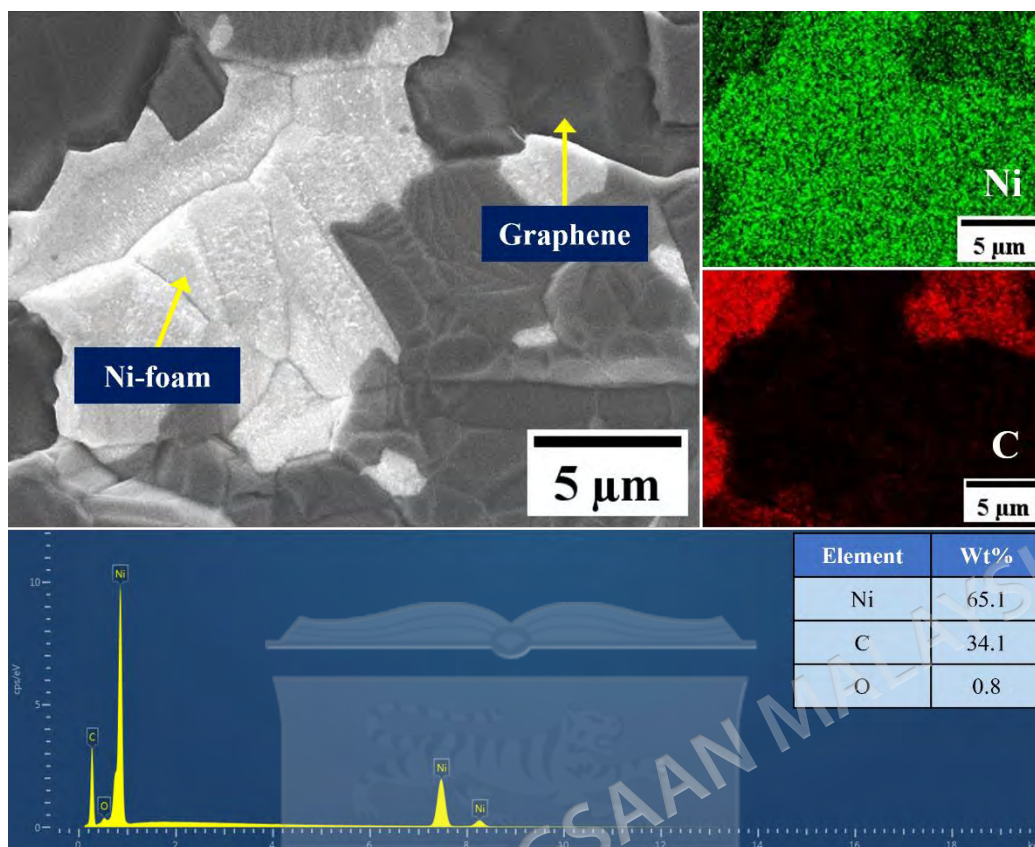


Figure 4.5 EDX mapping and elemental spectrum for graphene/Ni-foam at 50 minutes annealing time (CH_4 flow rate: 20 sccm, growth time: 30 minute).

The presence and quality of the synthesized graphene were further confirmed through Raman spectroscopy. As shown in Figure 4.6, increasing the annealing time resulted in nearly identical Raman spectral profiles across all samples. Two fingerprint peaks of graphene were clearly observed, the G band ($\sim 1581 \text{ cm}^{-1}$) and the 2D band ($\sim 2701 \text{ cm}^{-1}$) (Rosman et al. 2021). The G band refers to the in-plane stretching vibration of sp^2 -hybridization carbon atoms, while the 2D band corresponds to a two-phonon double resonance process. In addition, a slightly shift of the 2D band was observed across all samples. This peak shift is attributed to the presence of strain induced in the graphene. As noted in the FESEM discussion, this strain is from the difference in the thermal expansion coefficients between Ni and graphene, which generates internal stress during CVD reaction, as well as the lattice mismatch between Ni and graphene. Furthermore, the absence of the D band ($\sim 1350 \text{ cm}^{-1}$) in all samples indicates that the synthesized graphene is of high quality and free from defects (Goldie et al. 2020; Kang et al. 2018; Mohd Shah et al. 2022).

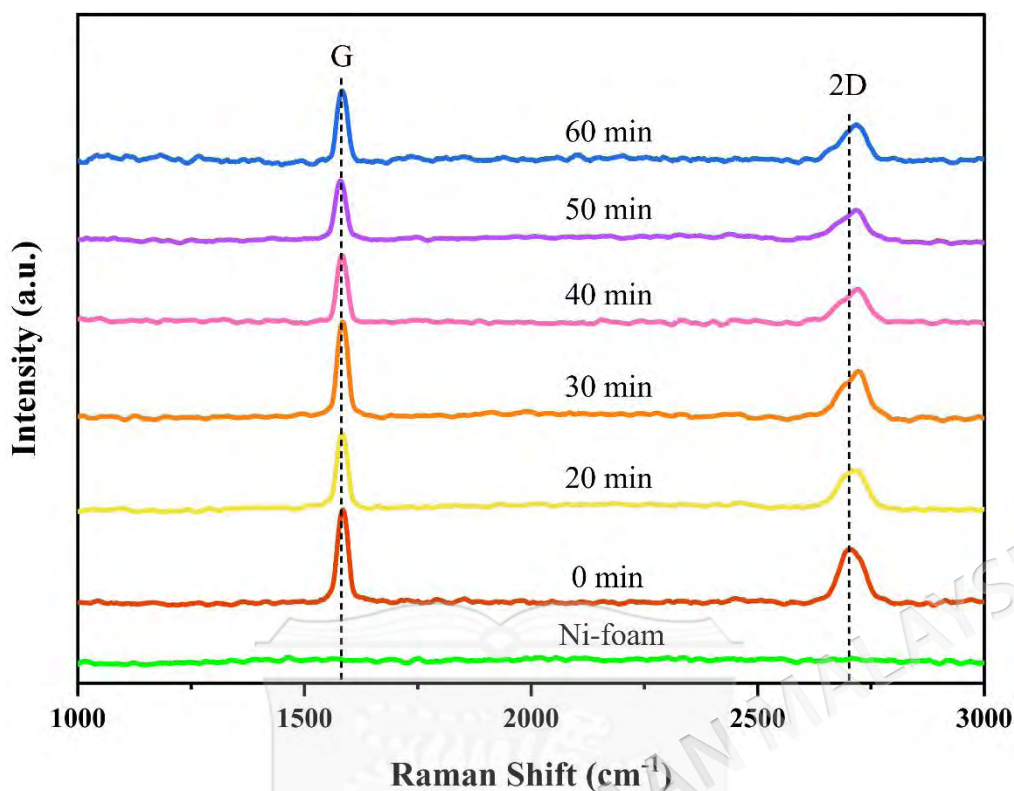


Figure 4.6 Raman spectra for graphene/Ni-foam at different annealing times (CH_4 flow rate: 20 sccm, growth time: 30 minute).

Additionally, the number of graphene layers for all samples was determined using the intensity ratio (I_{2D}/I_G), as shown in Figure 3.7 (Chapter III). Theoretically, an I_{2D}/I_G of ~ 2 represents single-layer graphene, a ratio of ~ 1 indicates double-layer graphene, values around 0.80 correspond to few-layer graphene, and a ratio of ~ 0.50 denotes multi-layer graphene. As tabulated in Table 4.2, the intensity of the G band is significantly higher than that of the 2D band across all samples. For 0- and 60 minutes samples, the I_{2D}/I_G ratio was slightly higher than 0.50, closer to few-layer graphene characteristics. In contrast, the samples annealed for 20 to 50 minutes showed an I_{2D}/I_G ratio is approximately 0.50. It shows clear characteristic of multi-layer graphene.

Table 4.2 The influence of annealing time on graphene/Ni-foam characteristics.

Annealing time (min)	I _{2D} /I _G value	I _{2D} /I _G layer category
0	0.57	Few-layer
20	0.49	
30	0.47	
40	0.48	
50	0.48	
60	0.50	Few-layer

Based on the FESEM, EDX, and Raman analysis, the best annealing time for graphene growth on Ni-foam substrate was determined to be 50 minutes. This duration resulted in the most uniform and highest coverage area of graphene on Ni-foam compared to the other samples. However, EDX mapping showed that there are uncoated Ni-foam areas, indicating that the H₂ reduction step remains a challenge in achieving full and homogeneous coverage on the Ni-foam substrate. Raman analysis confirmed the successful growth of graphene on Ni-foam, revealing a high quality with a few- and multi-layer graphene. Nevertheless, for photoelectrode applications, the graphene layer should ideally be as thin as possible, approaching a single layer graphene, to facilitate efficient electron transport (Tang et al. 2018). Therefore, the CH₄ flow rate will be adjusted to control the carbon supply, with the aim of achieving the thinner graphene layer on the Ni-foam.

4.3.2 CH₄ flow rates

Following the optimization of annealing time, the study was extended to investigate the effect of CH₄ flow rate in order to obtain the ideal, thinnest layer of graphene. Logically, as the number of graphene layers increases, electron must cross more layers or interfaces, which introduce interlayer scattering and hinder electron transport through the graphene thickness (Kumar et al. 2021; Tang et al. 2018). Therefore, controlling the graphene thickness by introducing CH₄ as carbon source is crucial for achieving optimal electron transfer properties. CH₄ is used to initiate the carbon dissolution process. Based on the previous results, an annealing time of 50 minutes and a growth time of 30 minutes were used, while the CH₄ flow rate was tailored from 0, 5, 10, 15, 20, and 25 sccm.

From the photo images in Figure 4.7, it is observed that the colour of the Ni-foam changes after the growth process, gradually changing from metallic grey (Ni-foam) to brownish at 0 sccm, followed by a mixture of brown and black at 5 sccm, and then slowly turning completely black for flow rates between 10 to 25 sccm. This darkening correlates with the increasing density and thickness of the deposited graphene.

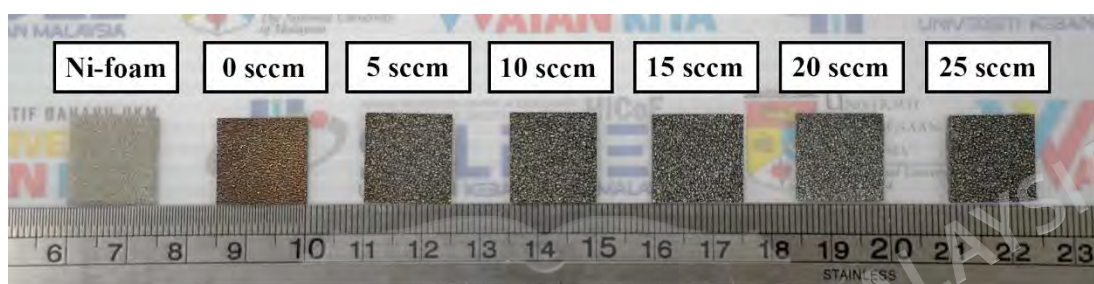


Figure 4.7 Photo images of graphene/Ni-foam showing the colour changes as CH_4 flow rate increase (annealing time: 50 minute, growth time: 30 minute).

As shown in the FESEM images in Figure 4.8 (a), the surface of the Ni-foam CH_4 supply (0 sccm) becomes rougher than pure Ni-foam. This is likely attributed to surface modifications and thermal etching occurring during the annealing step in the absence of CH_4 , as explained in Section 4.3.1. Furthermore, the graphene coverage on Ni-foam became more homogeneous as the CH_4 flow rate increase from 5 to 25 sccm (Figure 4.8 (b-f)). At low flow rate (5 sccm), the amount of CH_4 for dissolution into the Ni-foam is limited. This result is expected in the formation of thinner or inhomogeneous layers of graphene because the Ni does not reach its carbon solubility limit. Meanwhile, at higher flow rates (up to 25 sccm), the CH_4 concentration is high at the Ni-foam surface facilitates rapid carbon dissociation. Thus, more carbon atoms to dissolve into the Ni-foam. During the cooling process, the extra dissolved carbon is become precipitated at the Ni-foam surface, resulting in thicker graphene layer (Ago et al. 2015; Kalita & Tanemura 2017).

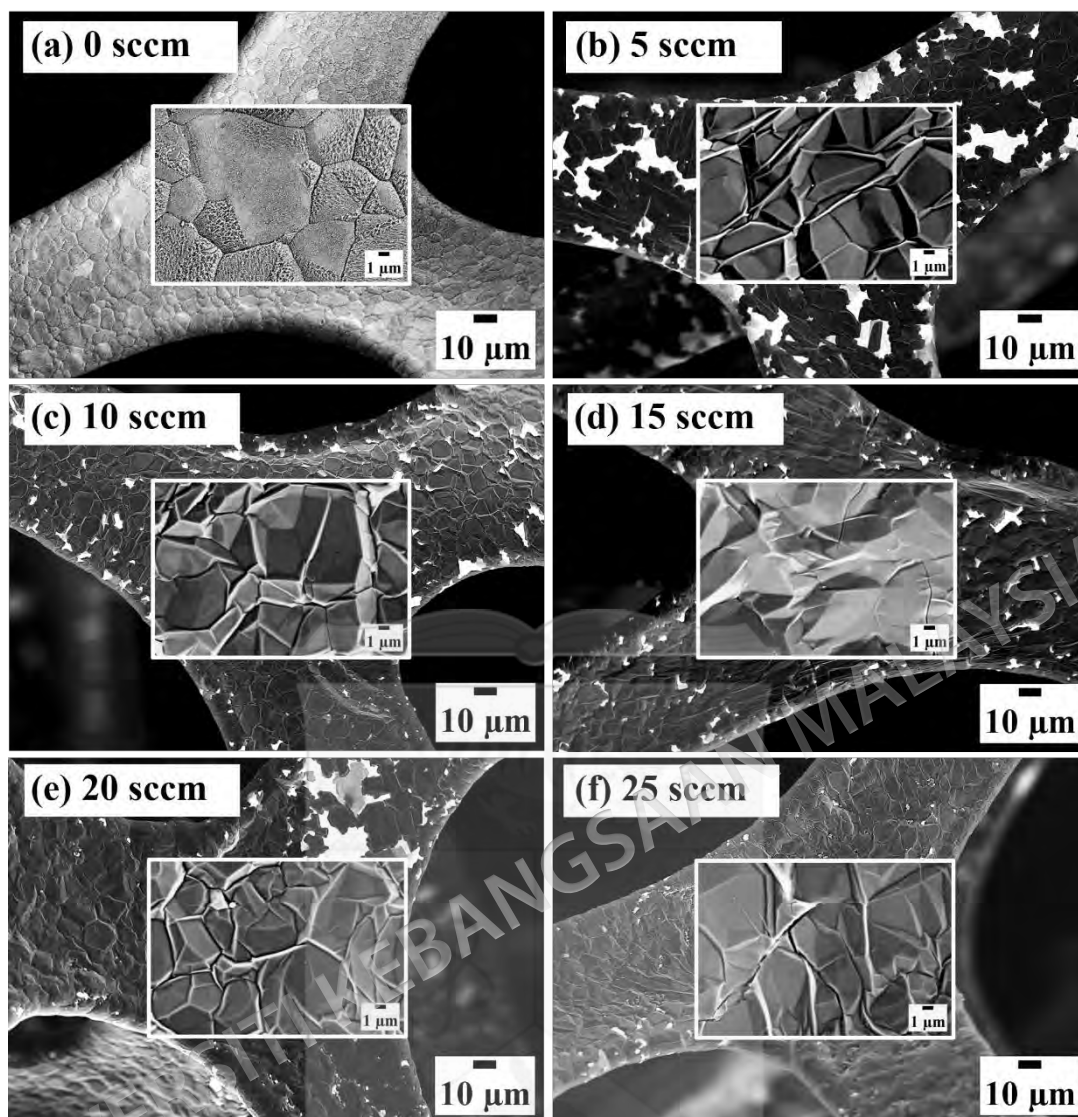


Figure 4.8 Low magnification (500x) FESEM images of graphene/Ni-foam at different CH₄ flow rates: (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, and (f) 25 sccm, with corresponding high magnification (5,000x) insets (annealing time: 50 minute, growth time: 30 minute).

Since the focus is to achieve the thinnest possible layer of graphene for enhanced electron transfer, FESEM cross-section analysis was performed on the 10 and 15 sccm samples, representing the intermediate flow rate range, to establish a thickness baseline and verify the growth trend. As shown in Figure 4.9, the 15 sccm sample exhibits a thicker graphene layer compared to the 10 sccm samples. This increase is directly attributed to the higher carbon flux provided by the increased CH₄ supply as a higher CH₄ flow rate leads to a higher volume of carbon atoms dissolving into and precipitating on the Ni-foam surface (Deokar et al. 2020). Hence, the 10 sccm sample appeared to offer the most favourable surface coverage and thickness.

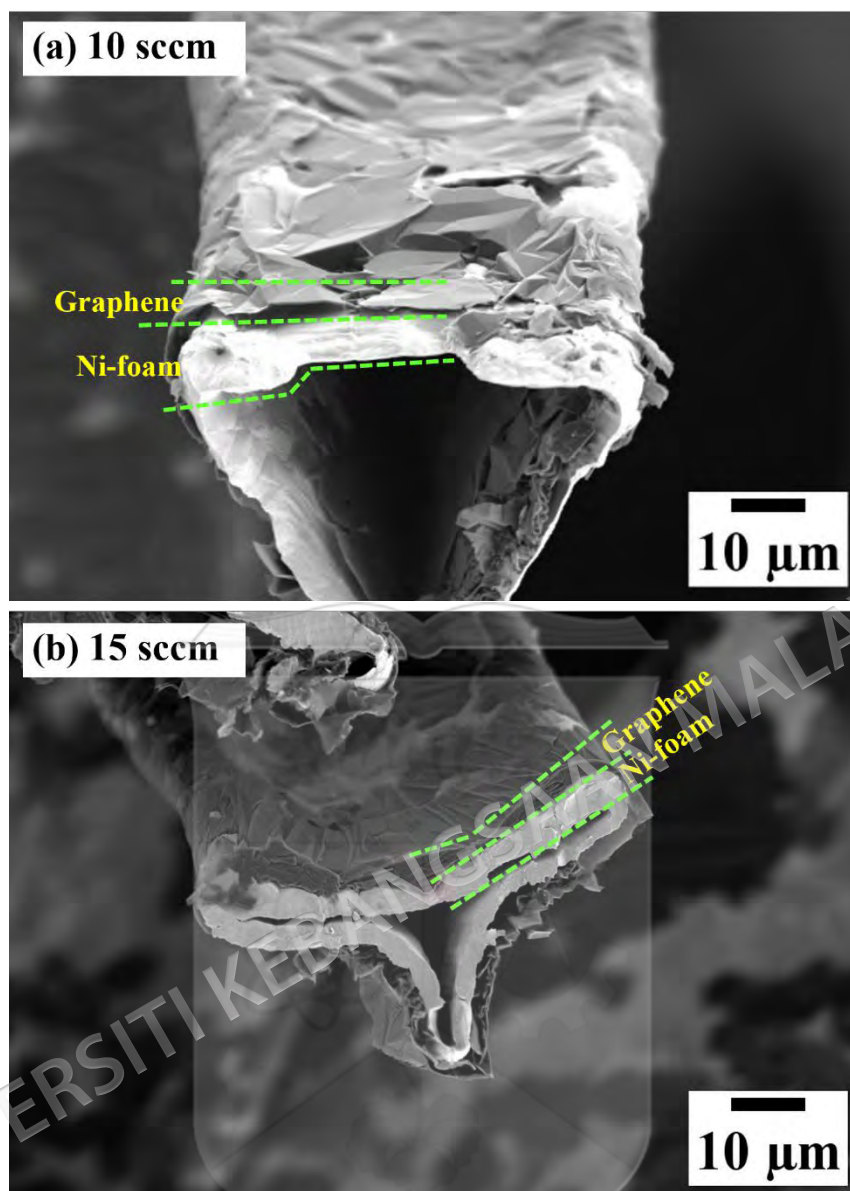


Figure 4.9 Cross-sectional FESEM micrographs of graphene/Ni-foam synthesized at (a) 10 sccm and (b) 15 sccm CH_4 flow rate (annealing time: 50 minute, growth time: 30 minute).

However, to precisely determine the number of graphene layers, Raman analysis was essential to confirm the suitable CH_4 flow rate to get the ideal thickness of graphene layer. As mentioned before, the number of graphene layers was determined using the I_{2D}/I_G intensity ratio, where ratios of ~ 2 , ~ 1 , ~ 0.8 , and ~ 0.5 correspond to single-layer, double-layer, few-layer, and multi-layer graphene, respectively. Figure 4.10 presents the Raman spectra of the graphene/Ni-foam synthesized at varying CH_4 flow rates. All samples exhibit a similar trend, where two characteristic peaks of graphene were identified, the G band at $\sim 1581 \text{ cm}^{-1}$ and the 2D band at $\sim 2701 \text{ cm}^{-1}$. Notably, the D

band at 1350 cm^{-1} is absent for all samples, confirming the high quality and low defect graphene (Goldie et al. 2020; Kang et al. 2018; Mohd Shah et al. 2022). The peak shift was observed only in the 2D band of the 20 sccm sample. This observation demonstrates that a CH_4 flow rate of 20 sccm induces localized compressive strain within the graphene lattice, primarily driven by the thermal expansion mismatch between Ni and graphene, rather than altering the graphene layer thickness (Anagnostopoulos et al. 2018). Interestingly, no peak shift was detected in the 2D band at the higher CH_4 flow rate of 25 sccm. This behaviour indicates that the excess carbon accumulation completely relaxes the structural strain through the micro-wrinkling or structural distortion of the graphene layers.

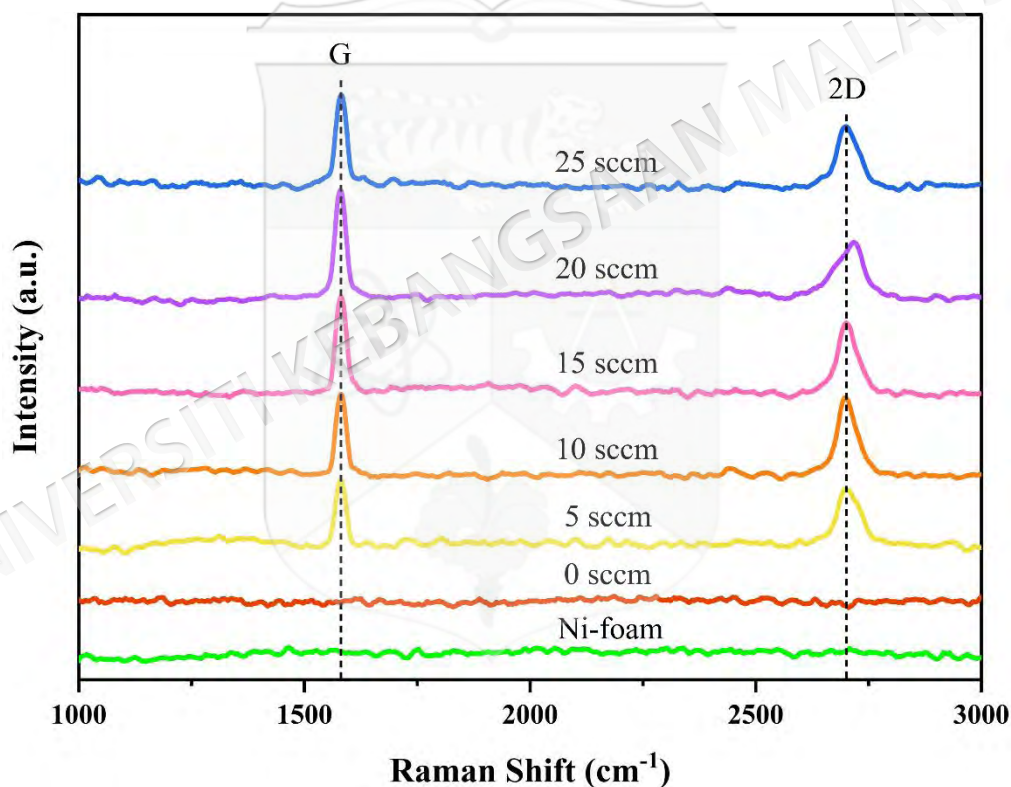


Figure 4.10 Raman analysis for graphene/Ni-foam at different CH_4 flow rates (annealing time: 50 minute, growth time: 30 minute).

In addition, the I_{2D}/I_G values obtained and listed in Table 4.3. The results show that the 10 sccm sample corresponds to double-layer graphene, whereas the 5 sccm and 15 sccm samples produced few-layer graphene. At higher CH_4 flow rates of 20 and 25 sccm, the graphene formed into multi-layer graphene. This trend suggests that increasing the CH_4 flow rate beyond the 10 sccm offers excessive carbon deposition,

leading to thicker graphene layers. As the graphene thickness increases, it becomes more difficult for electron to move vertically (out-of-plane) through the layers (Haidari et al. 2020; Shen et al. 2018). This is because each additional layer acts as a barrier, creating interfacial resistance. Thus, the electron must overcome this higher interfacial resistance, which increases the probability of interlayer scattering. This behaviour not only hinders electron transport but also promotes $e^- - h^+$ recombination, which are unfavourable to PEC performance.

Table 4.3 The influence of CH₄ flow rate on graphene/Ni-foam characteristics (annealing time: 50 minute, growth time: 30 minute).

CH ₄ flow rate (sccm)	I _{2D} /I _G	I _{2D} /I _G layer category
0	-	-
5	0.73	Few-layer
10	0.88	Double-layer
15	0.61	Few-layer
20	0.44	Multi-layer
25	0.55	

These results clearly demonstrate that the thickness of the graphene layer is highly dependent on the CH₄ flow rate. Among the tested conditions, 10 sccm was identified as the best CH₄ flow rate, as it successfully produces double-layer graphene. This finding is supported by a various characterization technique, including photo images, surface and cross-sectional FESEM analysis, and Raman spectroscopy. However, in addition to annealing time and CH₄ flow rate, the CVD growth time is also a critical parameter for obtaining high-quality graphene growth on Ni-foam. Hence, the next stage of this study focuses on tuning the growth time to further enhance the structural quality and coverage of the graphene/Ni-foam.

4.3.3 Growth time

Following the optimization of the CH₄ flow rate for graphene growth on Ni-foam, it becomes necessary to evaluate the impact of CVD growth time on the resulting graphene properties. The growth time plays a critical role, as it directly affects the nucleation density, surface coverage, and structural quality of the synthesized graphene. This is because, an insufficient growth time may result in incomplete carbon deposition,

leading in poor graphene coverage and higher density of structural defects. On the other hand, longer growth times facilitate the precipitation of additional graphene layers, promoting the formation of multilayer graphene, which is not recommended. Therefore, while maintaining the previously optimized annealing time of 50 minutes and a CH₄ flow rate of 10 sccm, the growth time was altered at 0, 10, 20 and 30 minutes.

Based on Figure 4.11, the surface morphology of the 0-minute growth time sample (Figure 4.11 (a)) is similar to the 0 sccm CH₄ flow rate sample of graphene/Ni-foam (Figure 4.8 (a)). Both displays the morphology of the Ni-foam after annealing but before any CH₄ is introduced. As growth time increases from 10 to 30 minutes, graphene coverage on the Ni-foam improves as more carbon is deposited. However, this results to the formation of a thicker graphene layer. Notably, the 30 minutes sample exhibits clear signs of graphene peel off from the Ni-foam surface (circle in red in Figure 4.11 (d)). According to Sirat et al. (2017), longer growth times can lead to a decrease in grain density. This is likely caused by the prolonged exposure to the high temperature of 1000 °C, which can cause thermal stress at the graphene–Ni interface during the cooling phase. Furthermore, theoretical studies indicate that stacked graphene layers exhibit weak interlayer adhesion due to vdW forces (Bhimanapati et al. 2015). This weak bonding, together with the accumulated thermal stress, explains the poor attachment and peeling of the thicker graphene layers from the Ni-foam surface at longer growth times.

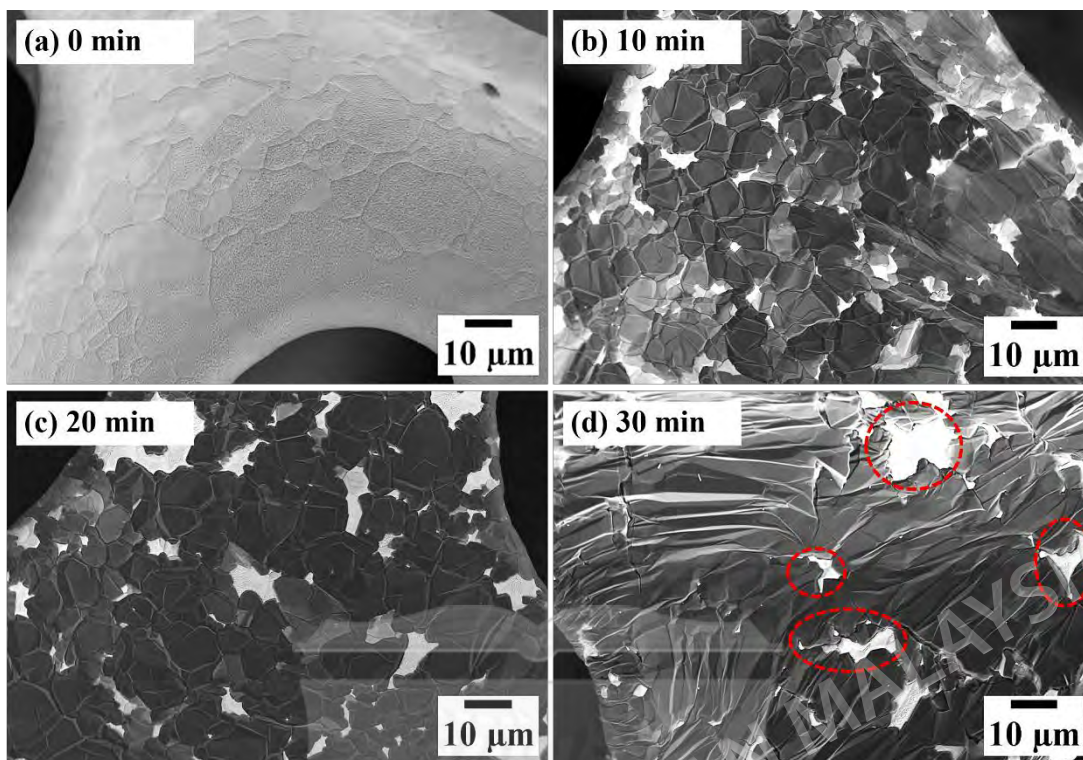


Figure 4.11 FESEM images of graphene/Ni-foam at (a) 0, (b) 10, (c) 20, and (d) 30 minutes growth times (annealing time: 50 minute, CH₄ flow rate: 20 sccm).

Consistent with the observations in the previous section, Raman analysis revealed two distinct graphene peaks at $\sim 1581\text{ cm}^{-1}$ (G band) and $\sim 2700\text{ cm}^{-1}$ (2D band). The D band was not detected in all samples, indicating that the synthesized graphene is high quality with minimal defects (Goldie et al. 2020; Kang et al. 2018; Mohd Shah, Rosman, et al. 2022; Rosman et al. 2021). As the growth time was extended from 10 to 30 minutes, the intensity of both the G and 2D bands increased (Figure 4.12). This suggests that even though the graphene layer remained constant, the structural quality improved and the coverage area of graphene on the Ni-foam surface became more homogeneous. Interestingly, all samples exhibit double-layer graphene characteristics, with I_{2D}/I_G value close to 1. As summarized in Table 4.4, the I_{2D}/I_G values were 0.92, 0.94, and 0.81 for 10, 20, and 30 minutes growth times, respectively. However, the decrease I_{2D}/I_G to 0.81 at 30 minutes growth time indicates a transition toward few-layer graphene, which show the limit where carbon over-precipitation begins to occur. This correlates with the observation from the FESEM image in Figure 4.11 (d), where the thicker layer of graphene starts to peel off from the Ni-foam.

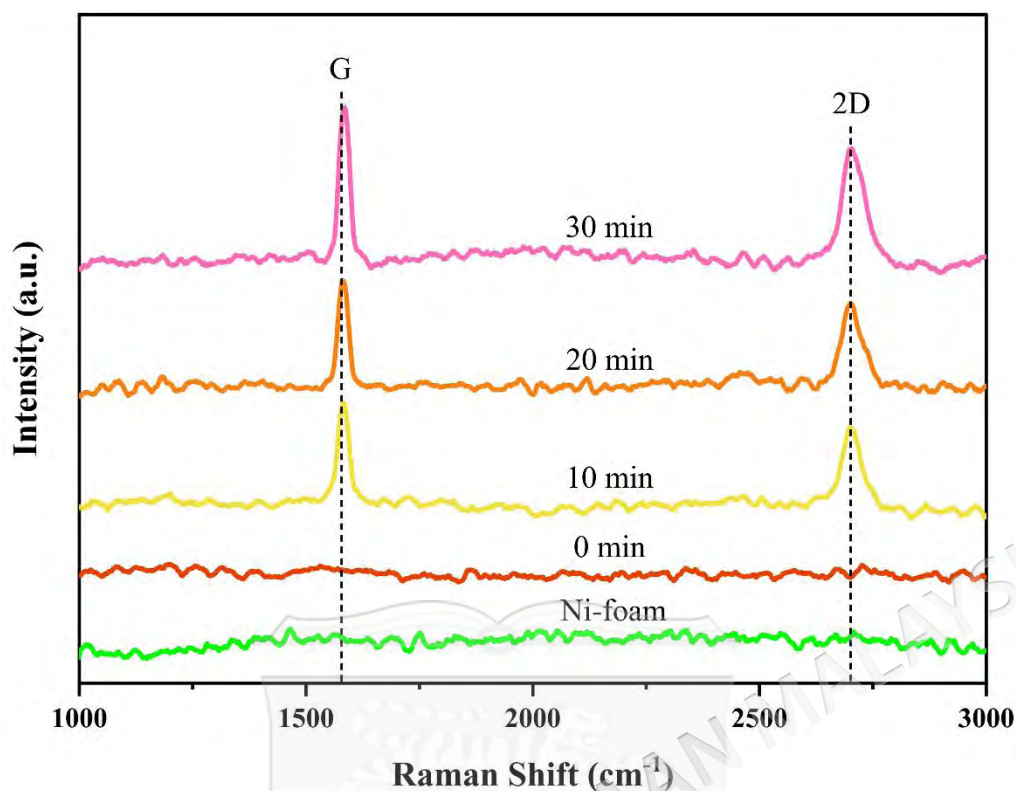


Figure 4.12 Raman spectra for graphene/Ni-foam at different growth times (annealing time: 50 minute, CH₄ flow rate: 20 sccm).

Table 4.4 The influence of growth time on graphene/Ni-foam characteristics (annealing time: 50 minute, CH₄ flow rate: 20 sccm).

Growth time (min)	I _{2D} /I _G	I _{2D} /I _G layer category
0	-	-
10	0.92	Double-layer
20	0.94	
30	0.81	Few-layer

For the 10- and 20-minute samples, the double-layer structure can be attributed to the carbon solubility limit of the Ni-foam substrate at 1000 °C. Once the Ni-foam is saturated with carbon atoms, the amount of carbon that precipitates to form graphene during the cooling process reaches a steady state. Consequently, longer growth times serve to enlarge the grain sizes and minimize the lattice defects between graphene and Ni rather than deposit more graphene layers. This explains why the G and 2D peak intensities increase while the I_{2D}/I_G ratio remains consistent with a double-layer structure. Hence, 20 minutes is identified as the best growth time for synthesizing high-quality graphene growth on Ni-foam via CVD method.

In conclusion, the systematic investigation into the influence of CVD parameters on graphene grown on Ni-foam substrate has established a precise procedure for synthesizing high-quality graphene. The optimization process revealed that an annealing time of 50 minutes, a CH₄ flow rate of 10 sccm, and a growth time of 20 minutes represent the most favourable conditions for this synthesis (Table 4.5). Comprehensive characterization confirmed the success of these parameters, where FESEM analysis verified a uniform, homogeneous, and well-coated graphene layer on Ni-foam surface, while Raman analysis indicated a high quality, defect-free double-layer graphene with I_{2D}/I_G ratio of 0.94. The identification of these parameters is important for PEC performance, as the ideal thickness of graphene layer that exhibits excellent surface coverage area with low interfacial resistance, helps in promoting efficient electron transport. As a result, this optimized graphene/Ni-foam acts as an ideal platform for the subsequent decoration of ZnO nanostructures as a photoelectrode.

Table 4.5 Optimized CVD parameters for synthesis graphene on Ni-foam.

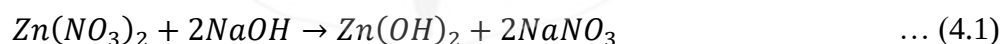
CVD Parameter	Optimum value	Main outcome
Annealing time	50 minutes	Pre-treatment of Ni-foam surface to facilitate graphene growth
CH ₄ flow rate	10 sccm	Controls carbon deposition to maintain a stable double-layer thickness
Growth time	20 minutes	Almost uniform and homogeneous graphene coverage

4.4 INFLUENCE OF ZnO MORPHOLOGICAL EVOLUTION ON THE PEC PERFORMANCE OF ZNO/GRAPHENE/NICKEL FOAM

Following the successful growth of graphene on Ni-foam, ZnO was deposited using the hydrothermal method to obtain ZnO/graphene/Ni-foam. This approach was chosen due to its simplicity, scalability, and the ability to precise control the ZnO morphology. By adjusting parameters such as reaction temperature and time, various ZnO nanostructures like nanorods, nanoflowers, or nanowires, can be synthesized. A significant advantage of the hydrothermal method is its low reaction temperature (typically below 200 °C), which preserves the structural integrity of the graphene/Ni-foam substrate. Furthermore, this solution-based technique can make sure that the ZnO precursor can effectively penetrate the internal pores of the 3D Ni-foam structure. This helps to form a uniform coating of ZnO on graphene/Ni-foam, providing a high surface area for

enhanced PEC performance. This reaction was conducted within a high-pressure autoclave, where the chemical reaction between the ZnO precursor and the aqueous solvent was influenced by the reaction time and temperature. However, in this study, only reaction temperature was controlled, as it is the fundamental parameter of nucleation and growth kinetics to determining the morphology and structural properties of the ZnO nanostructures.

Previous research has demonstrated that the hydrothermal synthesis of ZnO is highly temperature-dependent, with reaction temperatures significantly affect the morphology and structure of ZnO (Mohan et al. 2020). As previously mentioned, the hydrothermal reaction temperatures were modified from the methods from Mohan et al. (2020) and Ejsmont & Goscianska (2023) to facilitate the successful direct growth of ZnO directly onto the graphene/Ni-foam. Accordingly, temperatures of 150, 180, 190, 200 and 220 °C were investigated at a fixed reaction time of 8 hours to evaluate the influence on ZnO surface morphology and structural properties of ZnO after growing directly on graphene/Ni-foam. The resulting ZnO/graphene/Ni-foam are denoted as ZGNF-T, where T = 150, 180, 190, 200, and 220 °C. The $Zn(NO_3)_2 \cdot 6H_2O$ served as the Zn^{2+} precursor and NaOH as the source of hydroxide ions (OH^-). The synthesis proceeds by the formation of a $Zn(OH)_2$, which subsequently dehydrates to form stable ZnO, as described by the following mechanism (Biron et al. 2020; Koutu et al. 2016; Xiao et al. 2014):



The hydrothermal reaction time was maintained at 8 hours based on findings by Idiawati et al. (2017), which suggested that this reaction time provides sufficient thermal energy to achieve excellent crystallinity and optimal growth density for high-performance PEC applications. The mechanism of hydrothermal method was illustrated in Figure 4.13

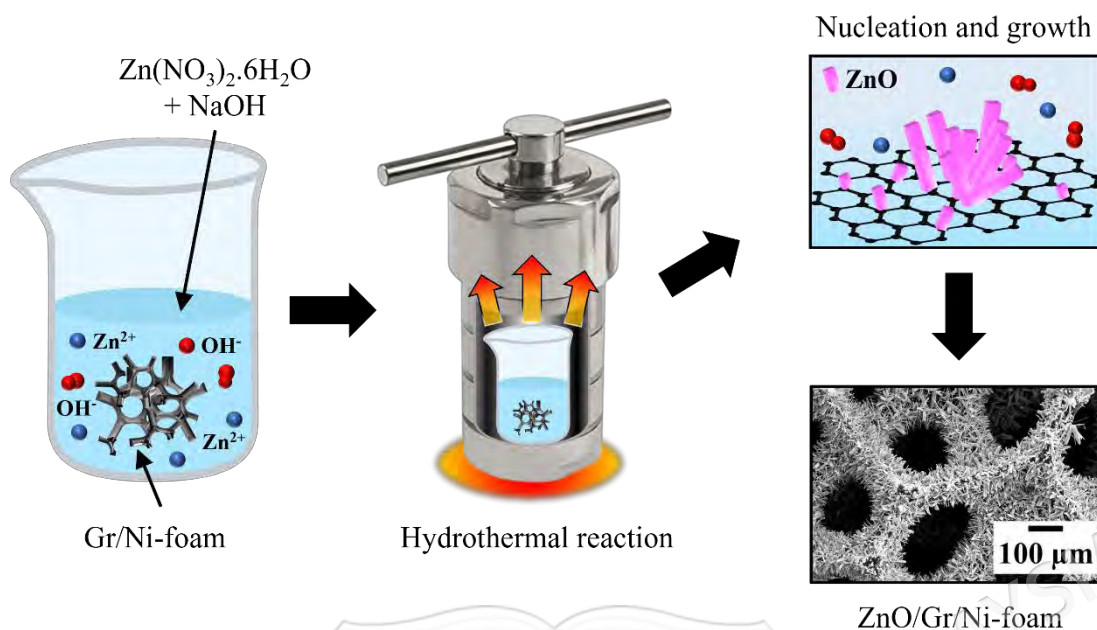


Figure 4.13 Schematic diagram of the hydrothermal synthesis for ZnO/graphene/Ni-foam (ZGNF).

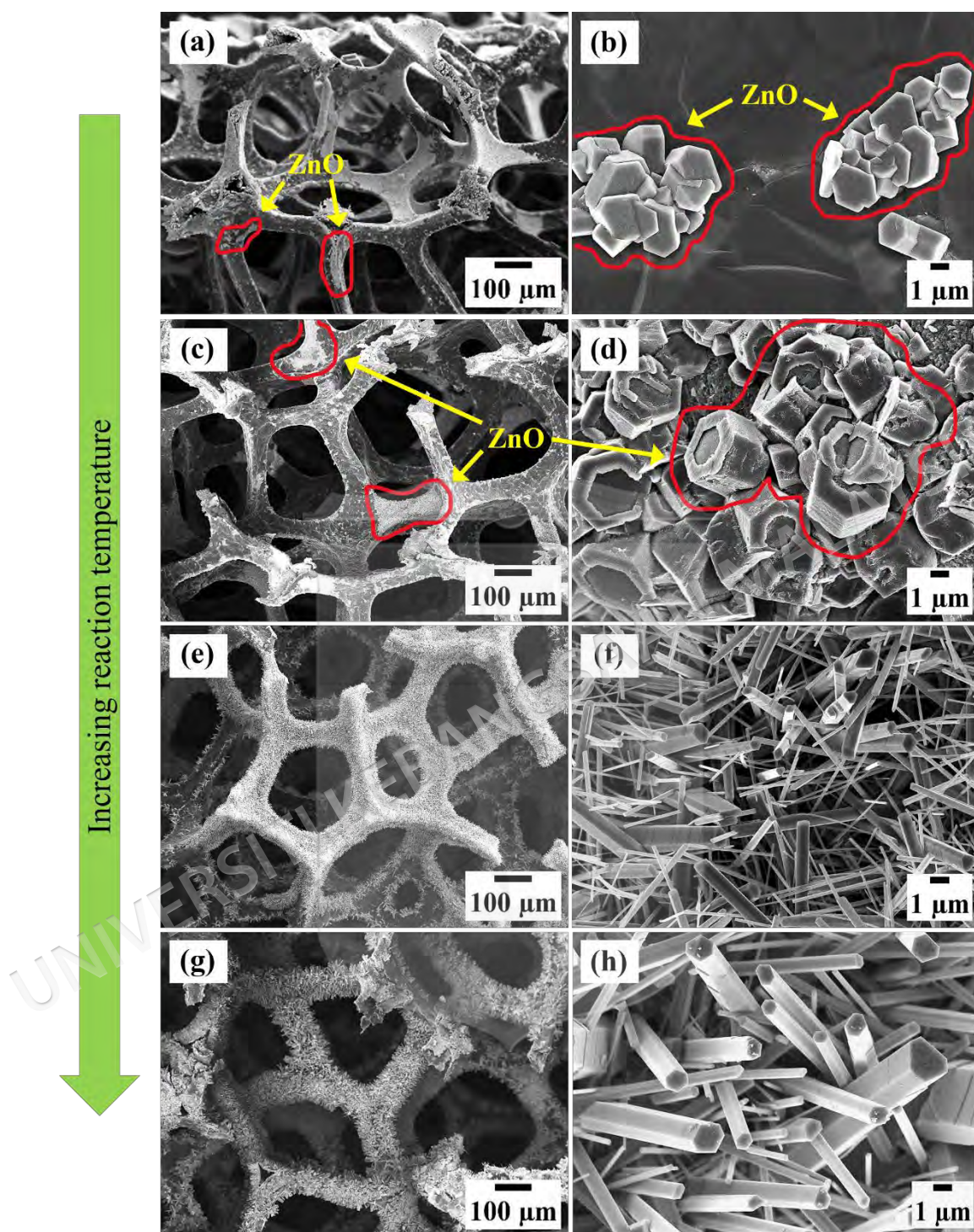
4.4.1 Surface morphology

The surface morphology and cross-sectional analysis of the ZnO/graphene/Ni-foam were conducted to investigate the influence of hydrothermal reaction temperature on ZnO growth. Figure 4.14 presents the FESEM images with the average length and diameter of ZnO on graphene/Ni-foam. A clear temperature-dependent trend was observed. As the reaction temperature increased from 150 °C to 220 °C, there was a proportional increase in ZnO surface coverage, length, and diameter. This occurs because higher hydrothermal temperatures provide excellent thermal energy, which enhances the diffusion rate Zn^{2+} and OH^- ions and increases the supersaturation of the growth solution. Hence, accelerates the nucleation and crystal growth kinetics of ZnO.

This morphological evolution is driven by the synergistic effects of hydrothermal reaction temperature and the role of NaOH. Thermodynamically, ZnO possesses an intrinsically anisotropic crystal structure with a highly polar [0001] c-axis, which promotes preferential crystal growth along this direction (Faisal 2016). At lower reaction temperatures (150 °C – 180 °C), the insufficient thermal energy limits the diffusion kinetics of the precursor species, restricting growth to localized nucleation sites. Consequently, ZnO coverage at 150 °C was minimal (Figure 4.14 (a, b)),

appearing as localized and scattered nucleation sites. This observation suggests that at this temperature, the ZnO has only just reached the activation energy required to initiate nucleation on the graphene/Ni-foam surface. As the temperature is increased to 180 °C (Figure 4.14 (c, d)), the nucleation density improves, leading to more ZnO growth. Further increasing the temperature to 190 °C (Figure 4.14 (e, f)) provided sufficient kinetic energy to promote preferential solute deposition along the high-energy [0001] orientation, leading to the formation of rod- and needle-like structures.

In addition to temperature, NaOH plays an important role in regulating the crystallization process by acting as a mineralizer. The OH⁻ ions supplied by NaOH react with Zn²⁺ ions to form soluble zincate complexes, [Zn(OH)₄]²⁻, which serves as the primary growth units for ZnO formation (Koutu et al. 2016; Mohamed et al. 2019). At higher temperature, the increased thermodynamic driving force overcomes the activation barriers associated with lateral crystal growth. This process promotes the transformation from thin rod-like structures to thicker and more densely packed hexagonal rods, forming a continuous and uniform coating across the graphene/Ni-foam. Accordingly, further increasing the temperature to 200 °C (Figure 4.14 (g, h)) and 220 °C (Figure 4.14 (i, j)) results in a nearly complete and uniform coating of the ZnO on graphene/Ni-foam, successfully forming the ZnO/graphene/Ni-foam. Within these high temperature samples, the ZnO exhibited well-defined hexagonal rod-like structures, and it becomes more thicker on 220 °C compared to 200 °C. This morphological evolution and homogeneity of the coating were further confirmed by the EDX mapping in Figure 4.14 (k), which displays a uniform elemental distribution of Zn and O throughout the graphene/Ni-foam substrate.



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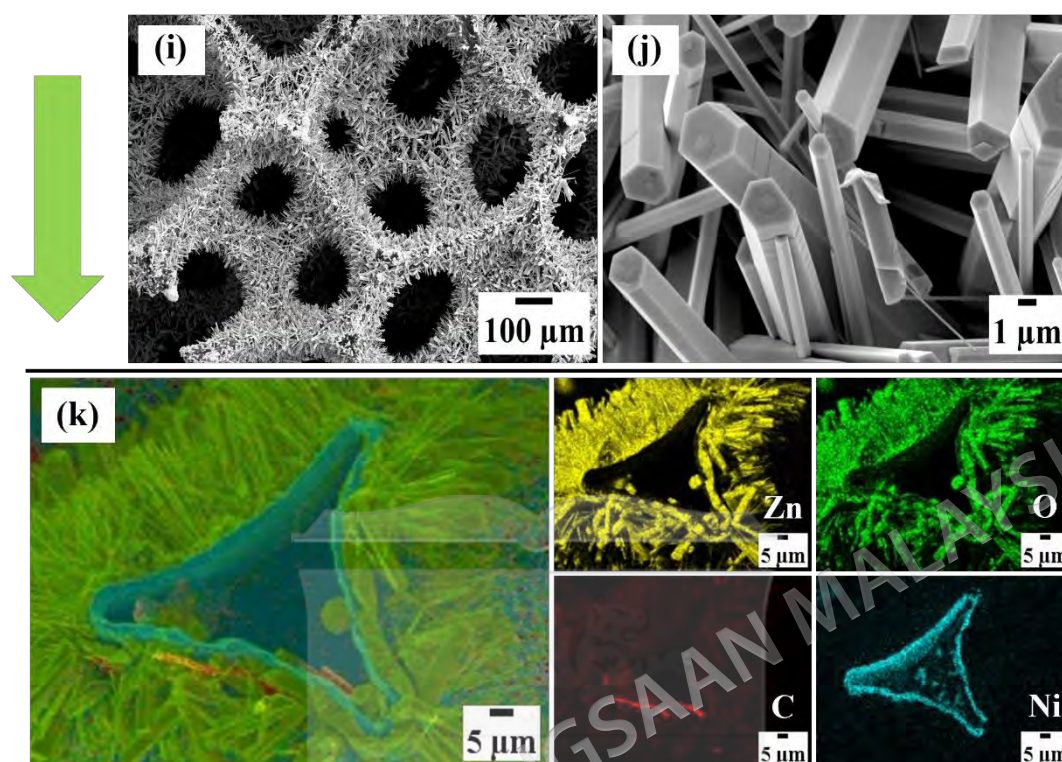


Figure 4.14 FESEM images at low (100x) and high (5,000x) magnifications of (a, b) ZGNF-150, (c, d) ZGNF-180, (e, f) ZGNF-190, (g, h) ZGNF-200 and (i, j) ZGNF-220. (k) EDX mapping of the ZGNF-200 sample.

To quantitatively analyse the morphological changes of the ZnO nanostructures, the length and diameter of the ZnO rods were measured from cross-sectional FESEM images using ImageJ software. For each sample, the average dimensions were obtained by measuring 10 representative nanorods (Figure 4.15). A systematic increase in both length and diameter was observed as the hydrothermal reaction temperature was increased. As summarized in Table 4.6, the measured dimensions follow the trend of ZGNF-220 > ZGNF-200 > ZGNF-190 > ZGNF-180 > ZGNF-150. Abdulrahman et al. (2021) investigated the influence of growth temperature on the morphological, structural, and light absorption properties of ZnO nanorods. The findings demonstrated that the aspect ratio (length-to-diameter) of the nanorods initially increased as the temperature increased but reduced at the highest temperature. Interestingly, light absorption continued to improve with increasing temperature despite the subsequent drop in aspect ratio. Similarly, in this study, samples synthesized at higher temperatures are expected to exhibit higher surface area, which can facilitate to

enhance light absorption and provide more active sites for water splitting reaction. From a morphological result, the ZGNF-190 and ZGNF-200 exhibits a high density of rods with excellent aspect ratio, while the ZGNF-220 shows the maximum nanorod length and diameter. Therefore, these three samples appear to be the most promising candidates for PEC applications owing to their high surface coverage and well-developed nanorods.

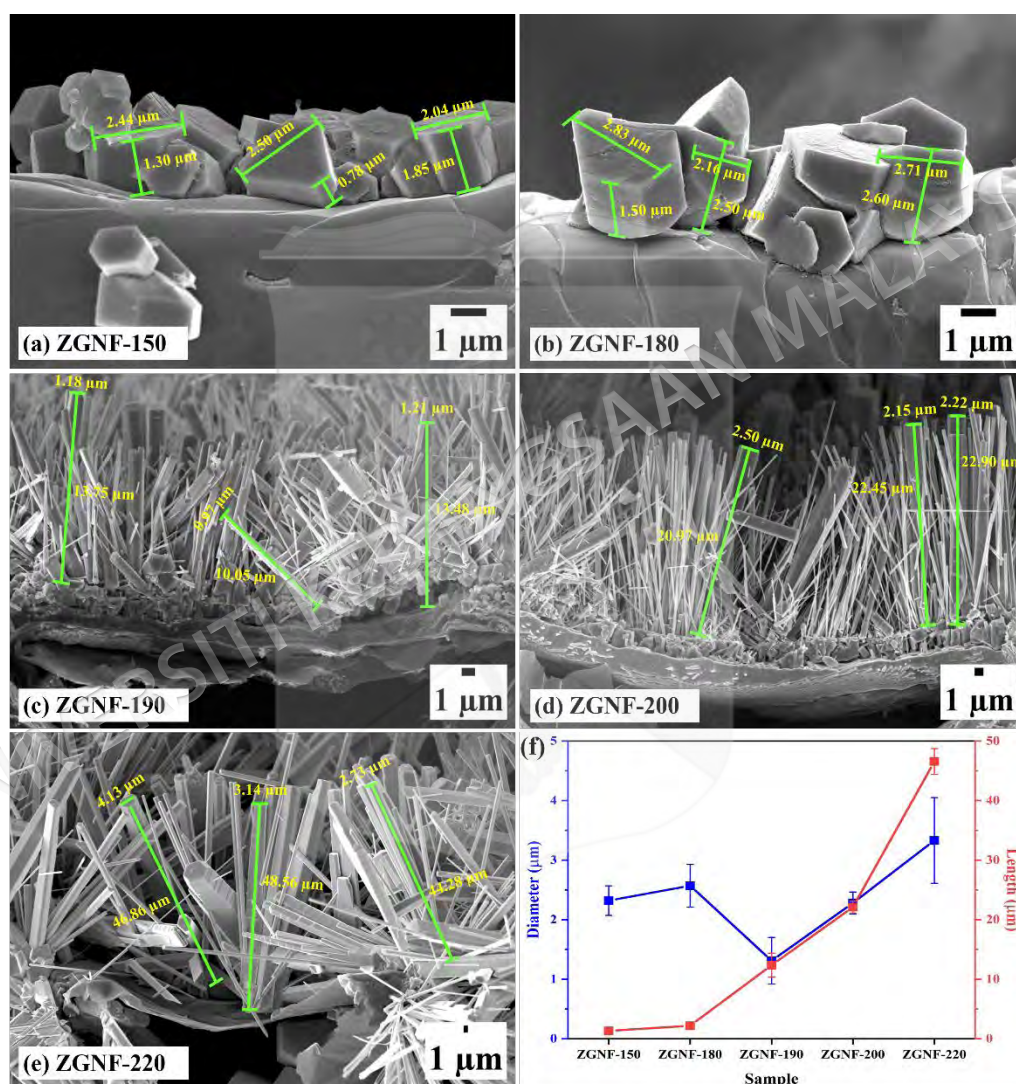


Figure 4.15 (a – e) Cross-sectional FESEM images of the ZnO/graphene/Ni-foam. (f) The average ZnO nanorods diameter and length at various reaction temperatures.

Table 4.6 Average dimensions of ZnO nanorods grown on graphene/Ni-foam at different hydrothermal reaction temperatures.

Sample	Length (μm)	Diameter (μm)
ZGNF-150	1.31	2.32
ZGNF-180	2.20	2.57
ZGNF-190	12.36	1.31
ZGNF-200	22.11	2.28
ZGNF-220	46.57	3.33

However, an excessive increase in nanorod diameter may reduce the specific surface area and influence the light-scattering properties of the photoelectrode. Therefore, while these high-temperature samples provide the most extensive surface area, their crystallinity, light absorption capability as well as the PEC performance must be evaluated. To investigate these physicochemical properties and to confirm the influence of reaction temperature on the structural characteristics of ZnO/graphene/Ni-foam, XRD analysis was carried out, as discussed in the following section.

4.4.2 Crystal structure

To investigate the crystalline phase and structural orientation of ZnO/graphene/Ni-foam synthesized at various hydrothermal reaction temperatures, XRD analysis was performed. The obtained diffraction spectra provide essential insights into the phase purity and crystallinity of the materials, which directly influence charge transfer and PEC efficiency.

As presented in Figure 4.16, three main peaks of Ni were clearly observed for all samples, at approximately $2\theta = 44.43^\circ$, 51.82° , and 76.39° , corresponding to the (111), (002), and (002) planes of the Ni-foam (PDF 98-006-2897) (Hu et al. 2019). Furthermore, the characteristic peak at $2\theta = 26.50^\circ$ corresponds to the (002) plane of graphitic carbon (PDF 98-005-3029) (Agudosi et al. 2020; Boruah et al. 2015), confirming the successful integration of graphene within the Ni-foam structure (inset Figure 4.16). Additionally, minor peaks at 38.32° and 65.09° are attributed to NiO (PDF 98-004-9131) (Liu et al. 2015). The presence of NiO is from the surface oxidation of the Ni-foam during the high-temperature annealing step of the CVD reaction or the subsequent hydrothermal treatment (Nordin et al. 2025). This finding strongly

correlates with the FESEM observations (Figure 4.4), which revealed that the Ni-foam was not fully coated with graphene, leaving the area exposed to oxidation. However, the NiO peak at 38.32° disappears after deposition of ZnO. This is likely due to the chemical etching of the Ni surface oxide layer within the hydrothermal growth solution.

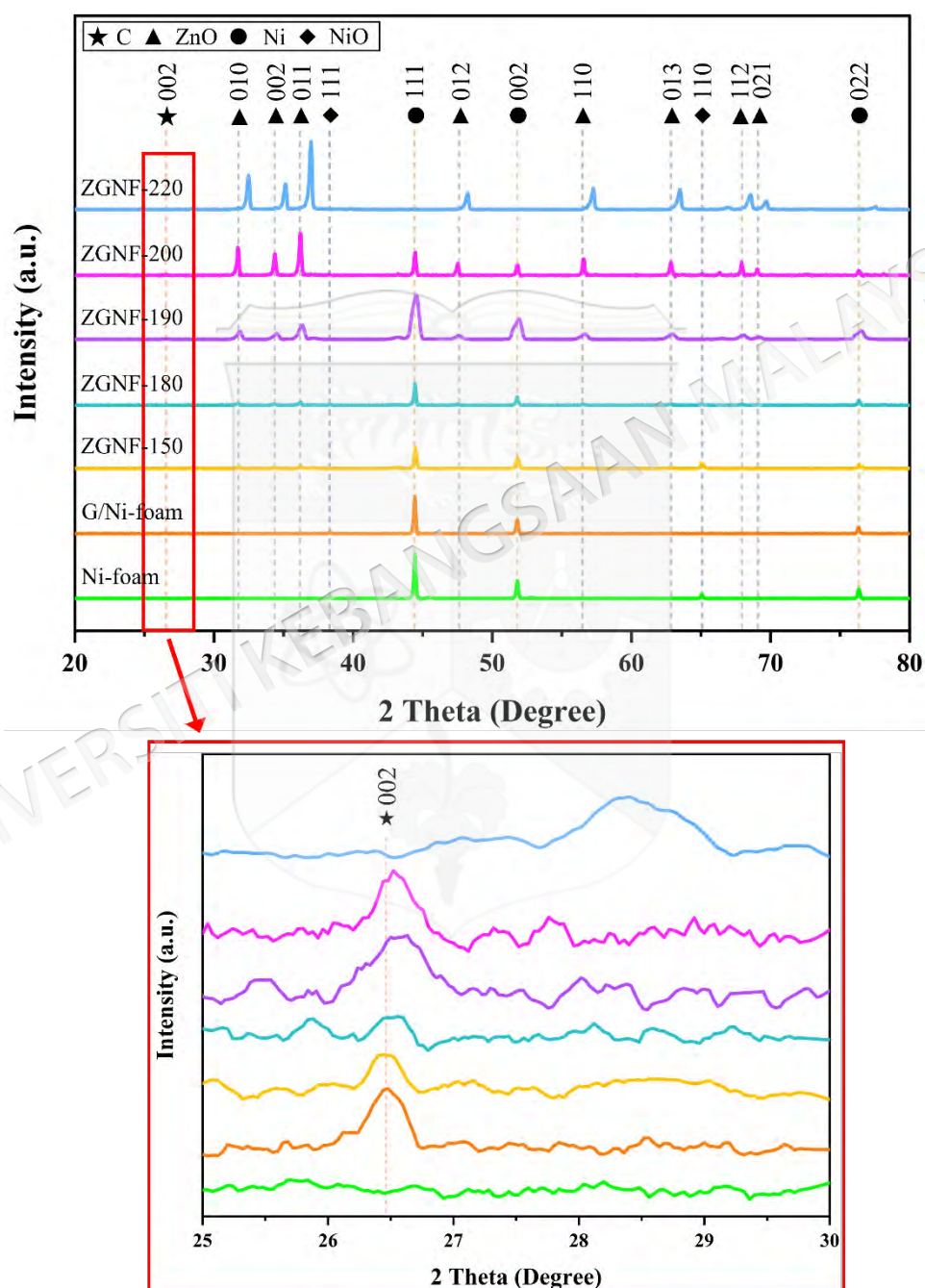


Figure 4.16 XRD patterns for Ni-foam, graphene/Ni-foam, and ZnO/graphene/Ni-foam synthesized at various reaction temperatures; the inset highlight the carbon peak at 26.50° .

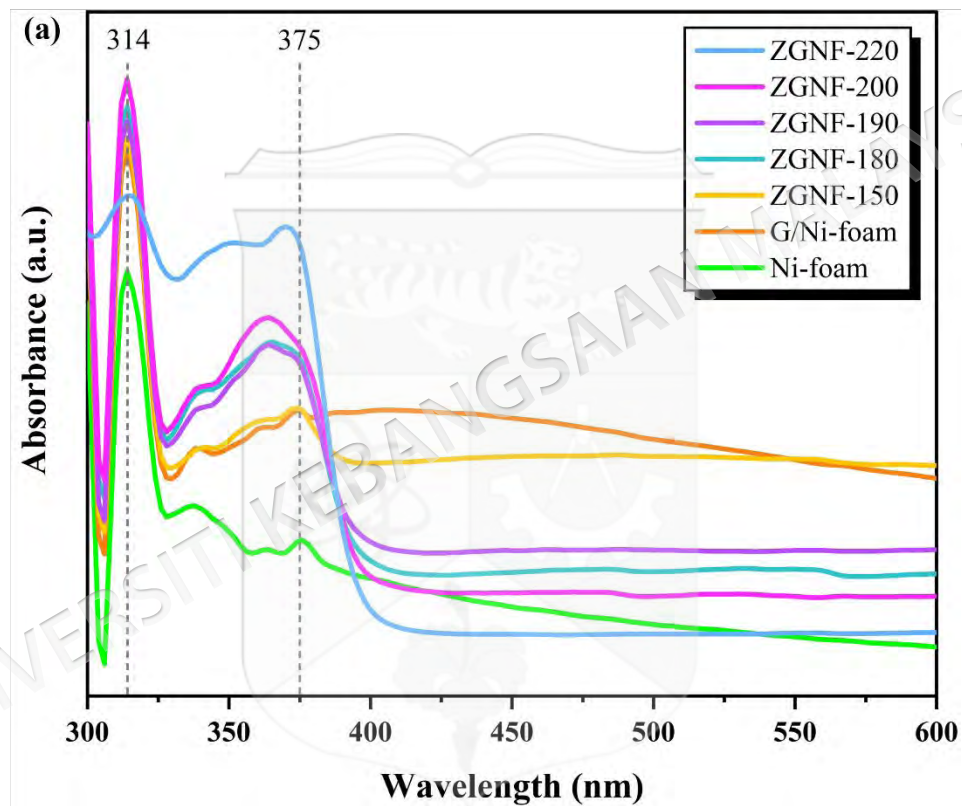
Regarding the ZnO growth, the diffraction patterns for ZnO clearly exhibit main peaks at 31.72° (010), 34.35° (002), 36.21° (011), 47.48° (012), 56.60° (110), 62.77° (013), 67.92° (020), and 69.04° (021) (Figure 4.16). These peaks are in good agreement with the hexagonal wurtzite structure of ZnO (PDF 98-006-5352) (Abdel-Rahman et al. 2021; Mohd Fudzi et al. 2018). Notably, the high intensity of (011) peak compared to other ZnO peaks shows that the ZnO nanorods preferentially grow along the yz-axis rather than strictly perpendicular to the graphene/Ni-foam surface. This behaviour is attributed to the 3D porous nature of the Ni-foam and the presence of graphene, which together facilitate the growth of nanorods in multiple directions (Zhang et al. 2019).

The influence of hydrothermal reaction temperature on the crystalline quality is evident through the variation in peak intensities. As the reaction temperature increased from 150°C to 220°C , the intensity of the ZnO peaks showed a significant increase. This trend indicates improved crystallinity and a higher density of ZnO on the graphene/Ni-foam, consistent with the increased coverage area and rod dimensions observed in FESEM (Figure 4.14 and Figure 4.15). Interestingly, a significant peak shift toward higher 2θ angles was observed for the ZGNF-220 sample. This shift indicates the presence of lattice strain within the ZnO wurtzite structure, likely induced by the increased thermal energy and lattice mismatch at higher synthesis temperatures. Since these structural characteristics affect the electronic properties of the ZnO/graphene/Ni-foam, their influence on the light absorption is further elucidated through UV-Vis characterization.

4.4.3 Light absorption

UV-Vis characterization was employed to investigate the light absorption behaviour of the ZnO/graphene/Ni-foam at various hydrothermal reaction temperatures. The absorption spectra were recorded between 300 – 600 nm, covers ultraviolet and visible light range. As shown in Figure 4.17 (a), all samples exhibit absorption peak at 314 nm, which indicates NiO formed on the Ni-foam (Joshna et al. 2019). However, the absorption peak intensity of NiO for the ZGNF-220 sample is lower due to the higher ZnO nanorods coverage that covers the surface of Ni-foam. Next, the absorption peak of ZnO for ZGNF-150 is observed at 375 nm, aligning well with the reported absorption

of bulk ZnO (Davis et al. 2019). However, a blue shift to 364 nm is observed for ZGNF-180, ZGNF-190, and ZGNF-200 (Baizae et al. 2018; Saputra et al. 2025). This shift usually suggests a widening of the intrinsic E_g due to lattice strain, which will be further reveal by Tauc plot derived from Equation (3.1). Then, the ZnO absorption peak of ZGNF-220 undergoes a slightly red shift to 369 nm. This behaviour supports the XRD results, suggesting that the lattice strain induced at higher temperatures, which effectively alters the electronic properties of the ZnO/graphene/Ni-foam.



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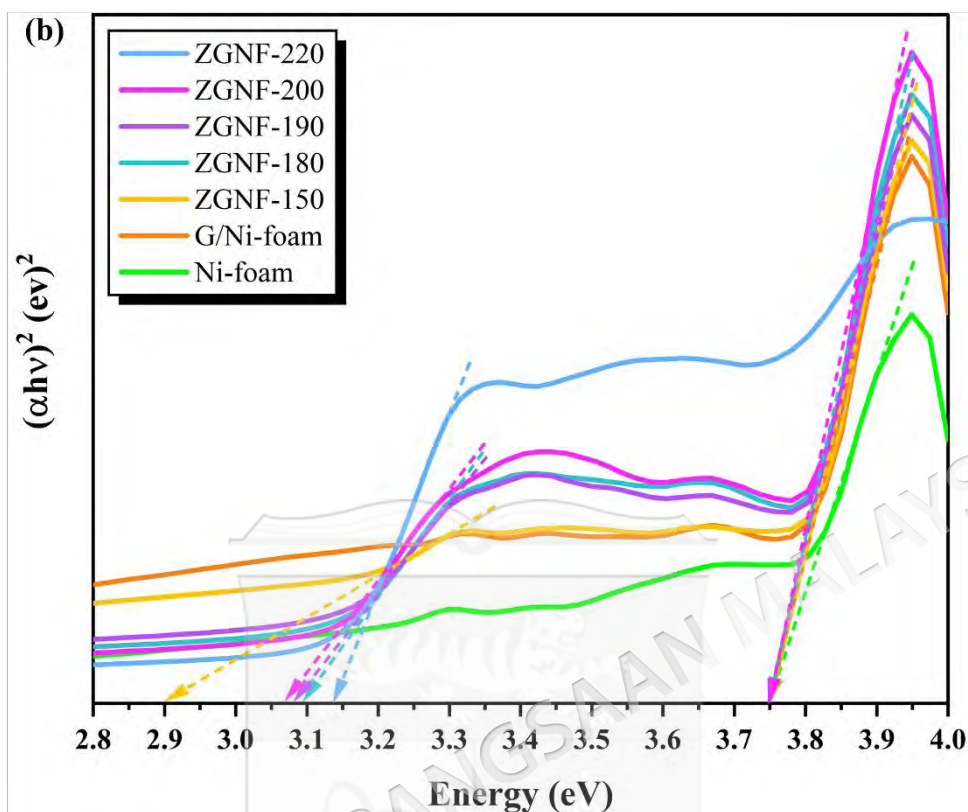


Figure 4.17 (a) UV-Vis spectrum and (b) Tauc plot for Ni-foam, graphene/Ni-foam, and ZnO/graphene/Ni-foam at various reaction temperatures.

Figure 4.17 (b) illustrates that the E_g values extrapolated from the Tauc plots follow the order: 2.90 eV (ZGNF-150) < 3.08 eV (ZGNF-200) < 3.09 eV (ZGNF-190) < 3.09 eV (ZGNF-180) < 3.14 eV (ZGNF-220). While a blue shift in absorption peaks usually corresponds to a widening of the E_g and a redshift to a narrowing E_g , these results show an inverse relationship. This behaviour is attributed to the synergistic interaction at the ZnO/graphene interface as well as background absorption from the Ni-foam substrate. The significantly lower E_g at 150 °C is likely associated by the presence of interfacial defects, which consistent with the low ZnO coverage area observed on the graphene/Ni-foam (Ayoub et al. 2022).

In contrast, increasing the hydrothermal temperature to 180 – 200 °C provides sufficient thermal energy to allow atomic rearrangement into a more ordered crystalline lattice, reducing defect-state (Abdulrahman et al. 2021). Furthermore, at 220 °C, a widening of the E_g is observed, which can be attributed to a combination of lattice strain and thermal defects associated with high temperatures (Kaushik et al. 2024). This structural behaviour aligns with the XRD peaks in Figure 4.16. Although some regions of the Ni-foam remain uncoated by ZnO or graphene, the density of defects is reduced at higher temperatures.

In addition, an E_g of approximately 3.75 eV was observed across all samples, indicating the existences of NiO in the ZnO/graphene/Ni-foam photoelectrodes (Joshna et al. 2019). The identical E_g values suggest that the NiO originates from the native oxide layer formed on the Ni-foam substrate. Since the Ni-foam substrate was utilized for all samples, the intrinsic electronic structure of the NiO layer remained unchanged. The contact between these two semiconductors creates an internal electric field at the interface and facilitates the separation of photogenerated $e^- - h^+$ pairs, where electrons move toward the NiO and holes toward the ZnO, significantly reducing charge recombination rates (Abdul Rahman et al. 2014).

Besides, graphene helps to extend the absorption into the visible light range and serves as an intermediate conductive bridge between NiO and ZnO, thereby improving the overall light absorption efficiency of the ZnO (Phuan et al. 2017). While this ZnO/graphene/Ni-foam structure facilitate rapid electron transport and contributes to a narrowing of E_g , this behaviour might be reduced in the ZGNF-220 sample. Due to the higher coverage and dense growth of ZnO nanorods, the NiO peaks is not detected, resulting in a wider E_g . Nonetheless, the synergistic effect within the ZnO/graphene/Ni-foam significantly broadens and enhances the light absorption capability of the material. The corresponding light absorption characteristics for all samples are summarized in Table 4.7.

Table 4.7 Summary of UV-Vis absorption peak positions and calculated band gap for ZnO/graphene/Ni-foam at various reaction temperatures.

Sample	Absorption peak (nm)		E_g (eV)		Reference
	NiO	ZnO	NiO	ZnO	
NiO	320	-	3.5 – 4.0	-	(Joshna et al. 2019)
ZnO	-	375	-	3.37	(Chia et al. 2025; ElFaham et al. 2021)
Ni-foam	314	-	3.75	-	This study
G/Ni-foam	314	-	3.75	-	
ZGNF-150	314	374	3.75	2.09	
ZGNF-180	314	364	3.75	3.09	
ZGNF-190	314	364	3.75	3.09	
ZGNF-200	314	364	3.75	3.08	
ZGNF-220	314	369	-	3.14	

4.4.4 PEC measurement

LSV and EIS were commonly used to evaluate the PEC performance of the photoelectrodes. In LSV measurements, the photocurrent is determined by subtracting the dark current from the light current response. It reveals the overall performance of the photoelectrode in terms of light absorption efficiency, charge separation capability, and charge transfer resistance. Meanwhile, EIS analysis provides insights into the interfacial properties, where a smaller semicircle radius in the Nyquist plot corresponds lower charge transfer resistance (R_{ct}) and more efficient electron transport. Hence, the combination of LSV and EIS provide a comprehensive understanding of the ZnO/graphene/Ni-foam structure for solar driven H_2 production. All result will be converted into RHE by using Equation (3.2).

Figure 4.18 presents the photocurrent density curves for the ZnO/graphene/Ni-foam samples. All samples exhibit a positive increase in photocurrent with increasing potential, confirming the n-type semiconducting behaviour of the ZnO/graphene/Ni-foam, where electron act as the majority carriers (Rosman et al. 2025; Sazali et al. 2024). This observation is further confirmed by Mott-Schottky analysis in the next section. The photocurrent density increases gradually as the hydrothermal reaction temperature increases from 150 °C to 200 °C, before decreasing at 220 °C.

At 1.23 V vs RHE, the photocurrent density was observed as: ZGNF-200 (29.04 mA/cm^2) > ZGNF-180 (18.68 mA/cm^2) > ZGNF-190 (18.01 mA/cm^2) > ZGNF-220 (15.17 mA/cm^2) > ZGNF-150 (8.87 mA/cm^2), as summarized in Table 4.8. This trend is closely related to the morphological structure of ZnO synthesized at different temperatures for 8 hours. In addition, the onset potential shifted to the lower potential (near to 0) as the reaction temperature increased. The outstanding performance of the ZGNF-200 sample is attributed to hexagonal rod-like morphology and high crystallinity. As illustrated in the FESEM images (Figure 4.15), this temperature produces an optimized nanorod density and length-to-diameter ratio, providing more active sites for efficient light absorption and PEC reaction.

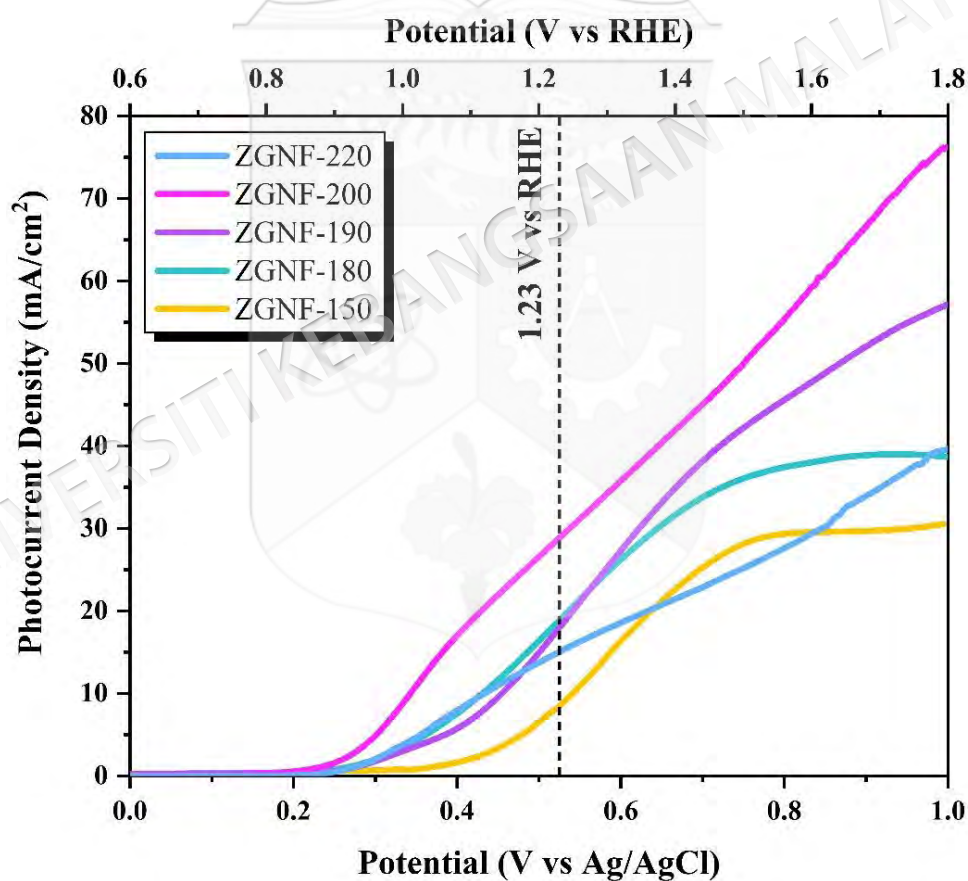


Figure 4.18 Photocurrent density graph of ZnO/graphene/Ni-foam at various hydrothermal reaction temperatures.

In contrast, as previously discussed in the FESEM analysis, the ZGNF-150 sample suffer from insufficient thermal energy for the complete nucleation and growth of ZnO. This poorly developed nanorods failed to provide enough light absorption and interfacial contact, resulting in the lowest photocurrent density. While the ZGNF-180 and ZGNF-190 samples showed an improvement, but their photocurrent densities remained limited by suboptimal nanorod density. Furthermore, the decrease in photocurrent density for the ZGNF-220 sample is attributed to the overgrowth of the ZnO nanorods. The thicker nanorods reduce the effective surface area available for the water oxidation reaction.

Next, EIS was performed under dark conditions to investigate the charge transfer kinetics and interfacial properties of the ZnO/graphene/Ni-foam photoelectrodes. In a Nyquist plot, the diameter of the semicircle arc represents the R_{ct} , where a smaller semicircle indicates lower resistance, allowing more efficient electron transport. As shown in Figure 4.19 (a), all ZnO/graphene/Ni-foam samples exhibit a semicircular arc, with the ZGNF-200 sample displaying the smallest diameter, followed by ZGNF-150, ZGNF-190, ZGNF-220, and ZGNF-180. This confirms that the 200 °C hydrothermal synthesis provides the most efficient pathway for charge movement by reducing the energy barriers at the interfaces compared to other temperatures.

To quantify these observations, the experimental data were fitted using the equivalent circuit as shown in Figure 4.19 (a). A CPE was incorporated into the fitting model to resolve dispersive capacitance and the non-ideal capacitive behaviour of across the surface of ZnO/graphene/Ni-foam. In this model, R_s represents the ohmic resistance, comprising the ionic resistance of the electrolyte and the series resistance of the graphene/Ni-foam, R_1 corresponds to the electronic charge transfer resistances at the internal interface between ZnO–graphene/Ni-foam, while R_2 represents the charge transfer resistances between photoelectrode–electrolyte interface. CPE1 and CPE2 serves as the corresponding dispersive resistance factors of R_1 and R_2 , respectively (Fareza et al. 2022; Rosman et al. 2025).

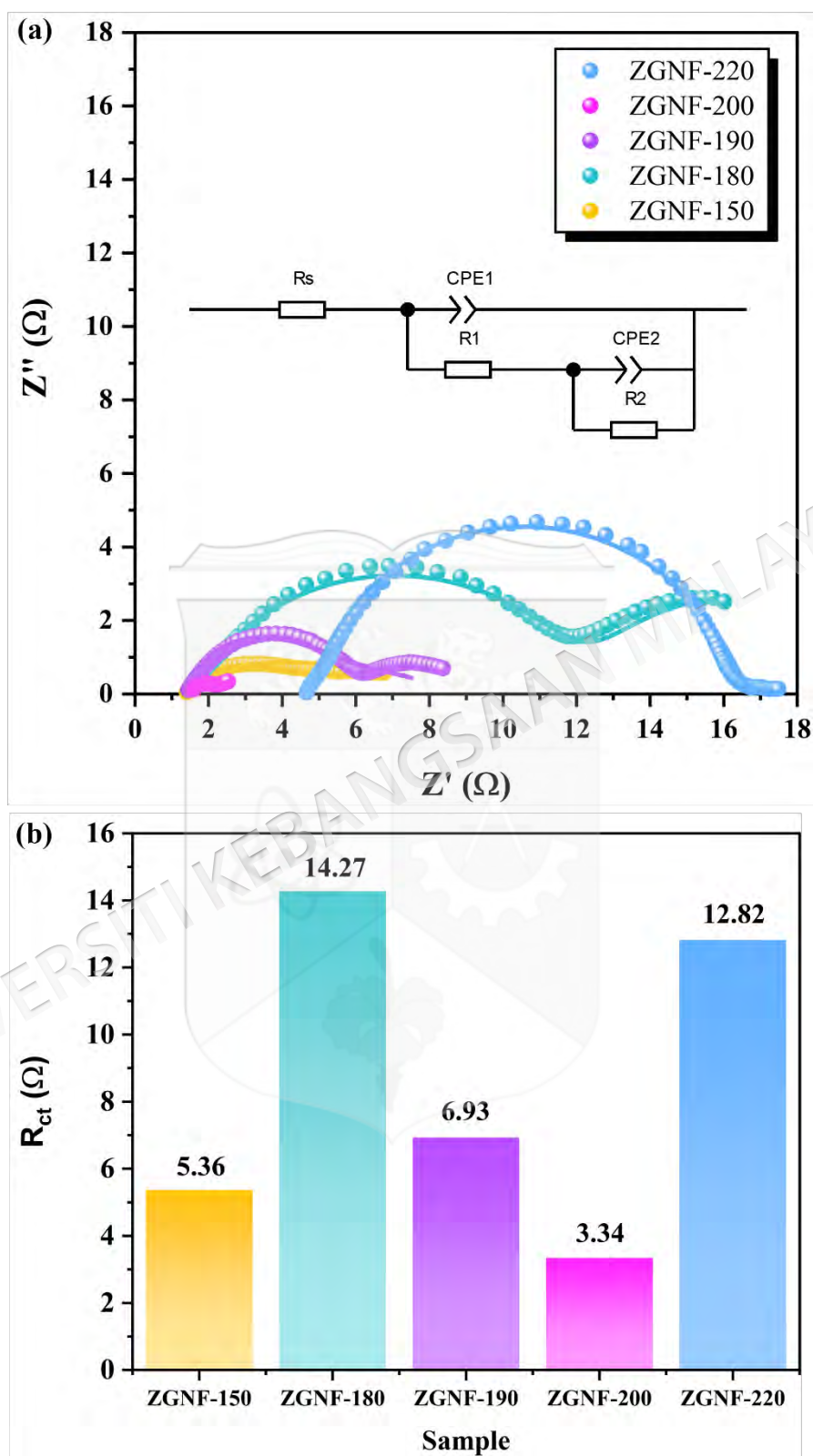


Figure 4.19 (a) Nyquist plots and equivalent circuit model for the ZnO/graphene/Ni-foam (the solid lines represent the fitting results) and (b) The corresponding R_{ct} at various reaction temperatures.

As can be seen in Figure 4.19 (b), the ZGNF-200 sample exhibits the lowest R_{ct} , indicating it possesses the smallest semicircle diameter among all samples. This finding supports by the calculated parameters in Table 4.8, which confirm that the ZGNF-200 sample yielded the lowest values for R1 and R2. The lowest R1 value suggests that the hexagonal rod-like morphology and high crystallinity achieved at ZGNF-200 have good interfacial contact with the graphene layer. This allows photogenerated electron to move from the ZnO to the graphene/Ni-foam substrate. Meanwhile, the lowest R2 value indicates that the high surface area and more active sites in the ZGNF-200 sample facilitate faster chemical reaction kinetics at the electrolyte interface. This synergistic effect results in efficient internal charge transport and rapid interfacial kinetics reaction, which explain why the ZGNF-200 sample achieved the highest photocurrent density in the LSV measurement.

Table 4.8 Summary of PEC performance and EIS parameters for all synthesized ZnO/graphene/Ni-foam samples.

Sample	Photocurrent Density (mA/cm ²)	Rs (Ω)	CPE	R1 (Ω)	CPE	R2 (Ω)	R _{ct} (Ω)
ZGNF-150	8.87	1.44	0.96	2.22×10^{-6}	0.32	6.36	5.36
ZGNF-180	18.68	1.51	0.68	10.95	0.70	8.33	14.27
ZGNF-190	18.01	1.48	0.98	1.48×10^{-6}	0.25	7.37	6.93
ZGNF-200	29.04	1.59	1.07	0.39	0.38	4.95	3.34
ZGNF-220	15.17	4.77	0.86	7.08×10^{-5}	0.12	12.59	12.82

Although the ZGNF-200 sample exhibited the best performance in both PEC and EIS measurement, a slight inconsistency was observed among other samples. Notably, ZGNF-180 exhibited the highest R_{ct} despite achieving the second-highest photocurrent density. This behaviour suggests that ZGNF-180 benefits from enhanced light absorption and more efficient photogenerated charge, driven by a smaller band gap (3.09 eV). However, the highest R_{ct} indicates slower interfacial charge kinetics, implying that photogenerated charge encounter higher resistance when injected into the Na₂SO₃ electrolyte. In contrast, ZGNF-150 samples showed lower R_{ct} than ZGNF-180 but produced the lowest photocurrent density. This observation suggests that although the incomplete growth of ZnO on the graphene/Ni-foam limits light absorption and overall charge transfer, these defects may reduce carrier mobility within the bulk material (Xue et al. 2021). While fewer surface states may facilitate charge transfer

across the interface, bulk defects and poor morphological coverage likely limit the photocurrent density. This highlights that the overall PEC performance is determined by a balance between charge generation efficiency and interfacial charge transfer kinetics.

The superior performance observed in the sample synthesized at 200 °C for 8 hours is attributed to the formation of a well-developed hexagonal rod-like morphology of ZnO. This one-dimensional (1D) structure increases the effective active surface area and provides a direct pathway for charge transport, significantly reducing the R_{ct} compared to the ZnO produced at 150 °C. Moreover, the decrease in photocurrent density at 220 °C indicates that the excessive thermal energy leads to crystal overgrowth or the formation of a dense and larger size of ZnO nanorods structures. These morphological changes likely result in a reduction of the effective active surface area and increase in bulk recombination sites, which hinder the migration of photogenerated $e^- - h^+$ pairs to the surface. Consequently, 200 °C is identified as the best hydrothermal reaction temperature for enhancing the charge separation efficiency and enhancing the PEC performance of the ZnO/graphene/Ni-foam.

In conclusion, the influence of hydrothermal reaction temperature for the formation of ZnO on graphene/Ni-foam was investigated in terms of the surface morphology, structural properties, and PEC performance. The synthesis temperature was found as the main factor that influenced the crystal growth behaviour, crystallinity, and the resulting charge transfer kinetics within the ZnO/graphene/Ni-foam. From the results, FESEM and EDX mapping confirmed the successful synthesis of ZnO using hydrothermal method. At the lower temperature (ZGNF-150 and ZGNF-180), the thermal energy was insufficient to promote dense nucleation, resulting in small dimension of ZnO and incomplete coverage on graphene/Ni-foam. For ZGNF-190, the ZnO nanorods did not fully cover the graphene/Ni-foam surface. In contrast, for ZGNF-200, the ZnO nanorods almost completely coated the entire surface of the graphene/Ni-foam with a suitable length and thickness, 22.11 μm and 2.28 μm , respectively. Furthermore, the coverage of ZGNF-220 remained high, but the ZnO nanorods became thicker due to excessive thermal energy. It shows that the temperature significantly

influenced the surface coverage and dimensions of these rods. In addition, XRD analysis shows that the crystallinity of the ZnO improved as the temperature increases.

UV-Vis spectroscopy revealed a synergistic effect between graphene and ZnO, resulting in a narrowed E_g of 3.08 eV at 200 °C compared to bulk ZnO (3.37 eV). This might be due to the presence of graphene modifies the electronic properties and the improve the light absorption efficiency of the ZnO. The E_g of NiO (3.75 eV) was observed due to the uncoated surfaces of the Ni-foam. Also, the PEC performance exhibited a clear temperature-dependent trend, where it shows that the photocurrent density increasing up to 200 °C before declining at 220 °C. The ZGNF-200 sample achieved the highest photocurrent density of 29.04 mA/cm² at 1.23 V vs RHE and the lowest R_{ct} of 3.34 Ω . This superior performance is attributed by the optimized hexagonal rod-like structure, which provides a high active surface area and facilitates rapid electron transfer through the graphene conductive bridge to the Ni-foam. Table 4.8

In short, the ZnO/graphene/Ni-foam is identified as a promising and efficient photoelectrode for PEC water splitting. The hydrothermal method provides a clear advantage in controlling ZnO growth on the graphene/Ni-foam substrate by adjusting the hydrothermal reaction temperature, which directly influences the morphology, structural properties, and PEC activity. It can be concluded that the ZGNF-200 sample, synthesized for 8 hours, exhibits the best PEC properties. Due to its superior photocurrent density and smaller interfacial resistance, this sample was selected for further characterization, including XPS, ABPE, Mott-Schottky, EIS, PEC, stability test and H₂ production, to provide a comprehensive evaluation of its potential for solar-driven H₂ production.

4.5 CHEMICAL BONDING AND PEC CHARACTERIZATION OF ZnO/GRAPHENE/NICKEL FOAM

As stated in previous section, the ZGNF-200 (denoted as ZnO/graphene/Ni-foam) was chosen for further investigation. The surface elemental composition, oxidation states, and chemical bonding of this sample were investigated using XPS. To identify the chemical shifts and interfacial interactions introduced by the hydrothermal method, the graphene/Ni-foam sample was used as a control. All E_b were calibrated to the adventitious carbon (C 1s) peak at 284.4 eV as reference (Mohamed et al. 2019). Figure 4.20 shows the wide scan survey spectrum for ZnO/graphene/Ni-foam and graphene/Ni-foam sample. Both samples confirm the presence of carbon (C 1s), oxygen (O 1s), and nickel (Ni 2p). Following the hydrothermal growth of ZnO on graphene/Ni-foam, the additional peaks for zinc (Zn 2p) were detected. This presence of zinc, oxygen, carbon, and nickel in the survey scan confirms the successful integration of all four components, consistent with the results obtained from the EDX and XRD analysis.

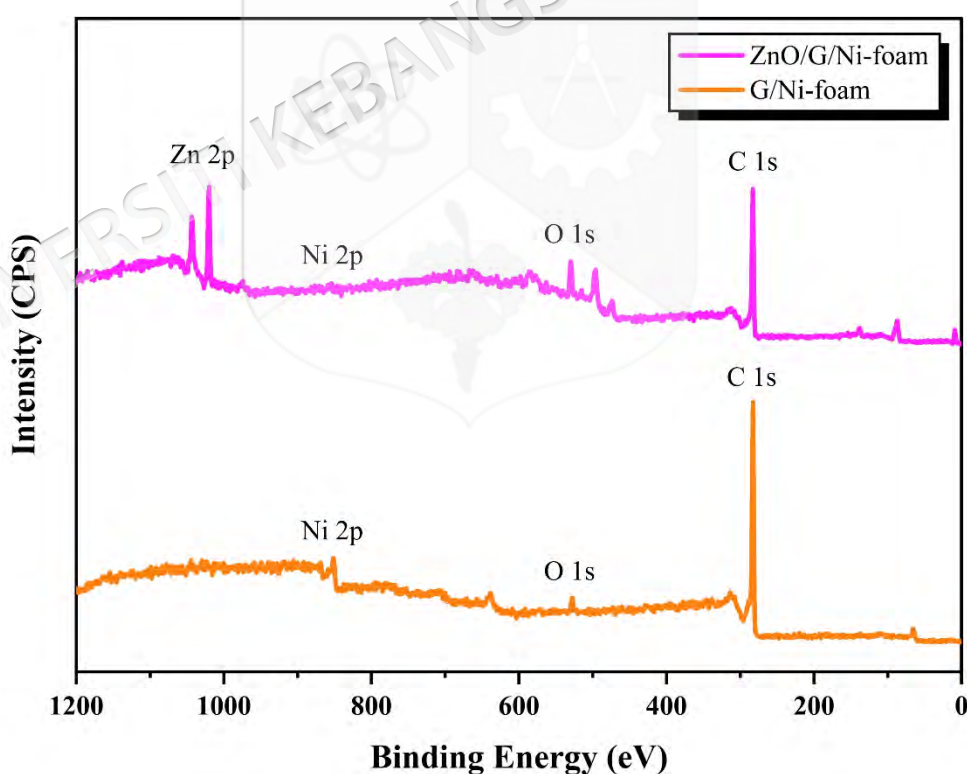
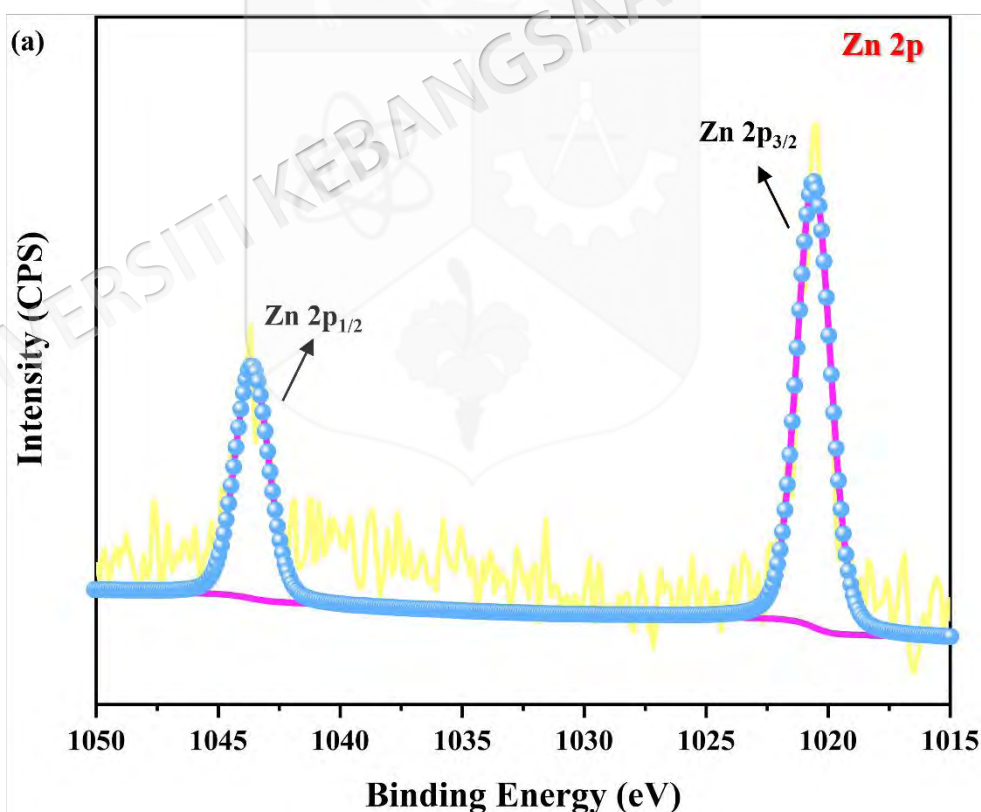


Figure 4.20 XPS survey spectra of the ZnO/graphene/Ni-foam and the graphene/Ni-foam.

The high-resolution Zn 2p spectrum (Figure 4.21 (a)) displays two symmetric peaks at 1043.68 eV and 1020.63 eV, corresponding to the Zn 2p_{1/2} and Zn 2p_{3/2} spin-orbit components, respectively. The spin-orbit splitting of approximately ~23.00 eV is consistent with the reported literature for the Zn²⁺ oxidation state in wurtzite ZnO lattice (Mohamed et al. 2019; Shakil et al. 2018; Tomić et al. 2021). The O 1s spectrum was deconvoluted into two peaks (Figure 4.21 (b)). The dominant peak at 530.10 eV is assigned to lattice O (ZnO-O). The difference in electronegativity between O ($X = 3.44$) and Zn ($X = 1.65$) facilitates a strong electrostatic interaction, wherein the O²⁻ ions are coordinated by Zn²⁺ cations to form the stable wurtzite ZnO phase. The second peak located at 525.01 eV is attributed to surface-adsorbed O species or C-O related bonds (Shakil et al. 2018). The interaction at this interface is important for the PEC performance, as these surface species can act as intermediate sites for the water oxidation reaction.



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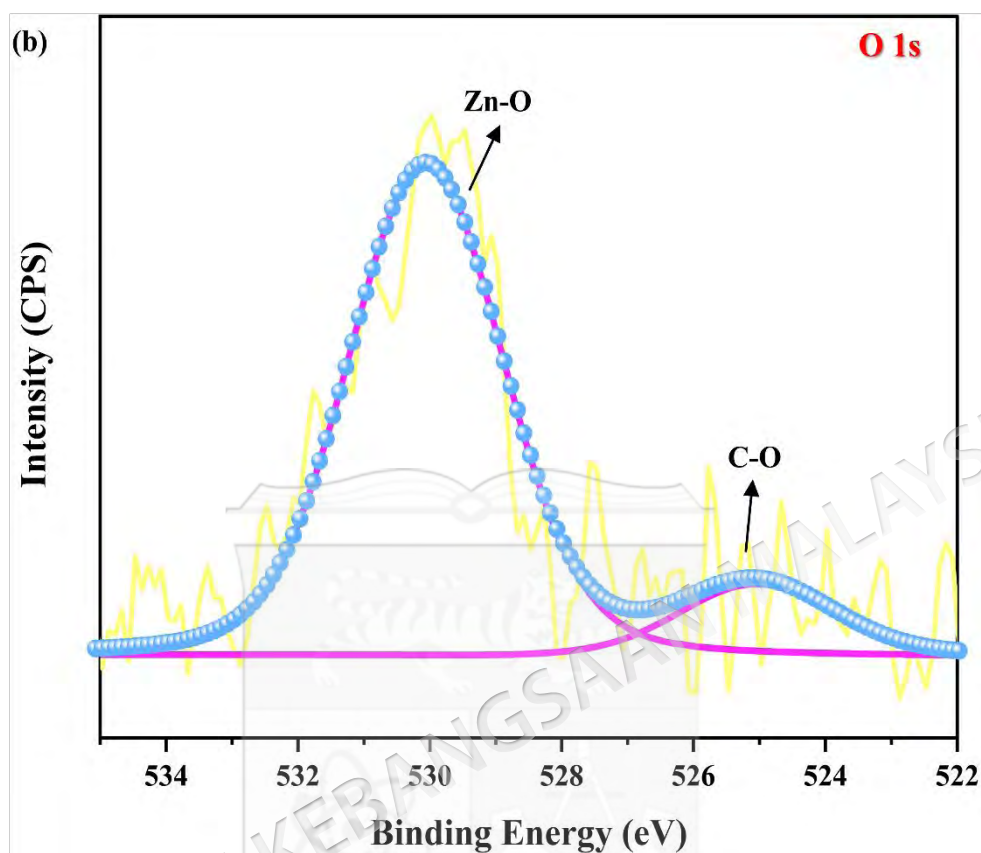


Figure 4.21 High-resolution XPS spectra of (a) Zn 2p and (b) O 1s for the ZnO/graphene/Ni-foam sample.

The deconvolution of the C 1s spectra (Figure 4.22) reveals four prominent peaks with a slight shift toward higher E_b after adding ZnO. Both samples exhibit peaks for C-C bonds (associated with sp^2 and sp^3 hybridized carbon) and Ni-C bonds, indicating a strong interfacial interaction between graphene and Ni-foam (Furlan et al. 2014; Gao et al. 2016; Yang et al. 2020). Notably, the C=C peak for graphene/Ni-foam appears at a lower E_b (282.92 eV), further confirming the electronic interaction between graphene layer and the Ni-foam substrate. Upon ZnO deposition, an additional Zn-C peak appears at 283.12 eV, indicating the presence of zinc carbide (Kim & Kim 2015). This suggests that carbon atoms partially occupy oxygen vacancies within the ZnO lattice. Due to the electronegativity difference between zinc ($X = 1.65$) and carbon ($X = 2.55$), these elements tend to form a polar covalent bond. The formation of this Zn-C is highly beneficial for PEC applications, where it facilitates efficient charge

transfer from the ZnO nanorods to the graphene conductive layer, effectively suppressing the recombination of photogenerated $e^- - h^+$ pairs (Beltrán et al. 2019; Kim & Kim 2015).

The high-resolution of Ni 2p spectra were analysed to evaluate the oxidation state of the graphene/Ni-foam and its interaction with ZnO, as shown in Figure 4.23. For graphene/Ni-foam sample, peaks were observed at 868.88 eV (Ni 2p_{1/2}) and 851.70 eV (Ni 2p_{3/2}), respectively, with corresponding satellites at 876.97 eV and 858.68 eV, respectively. The calculated spin-orbital energy difference was ~17.00 eV is in excellent agreement with the literature values for the metallic Ni phase (Pal et al. 2015; Shakil et al. 2018). For ZnO/graphene/Ni-foam, the E_b shifted to 874.70 eV (Ni 2p_{1/2}) with the satellite peak at 882.63 eV and 850.52 (Ni 2p_{3/2}) with the satellite peak at 861.07 eV. This shift is attributed to the modification in the electronic properties of the graphene/Ni-foam due to the interfacial interaction with the ZnO nanorods (Mou et al. 2021). It should be noted that fitting the Ni 2p peaks is challenging because XPS can only detect about 10 nm of the surface (Krishna & Philip 2022). As the Ni-foam is covered with the ZnO and graphene, the photoelectrons emitted from the underlying Ni are partially attenuated by the overlayer. These findings confirm the successful chemical integration and strong interfacial contact between ZnO, graphene, and Ni-foam, which are essential for the efficient separation and transport of photogenerated $e^- - h^+$ pairs.

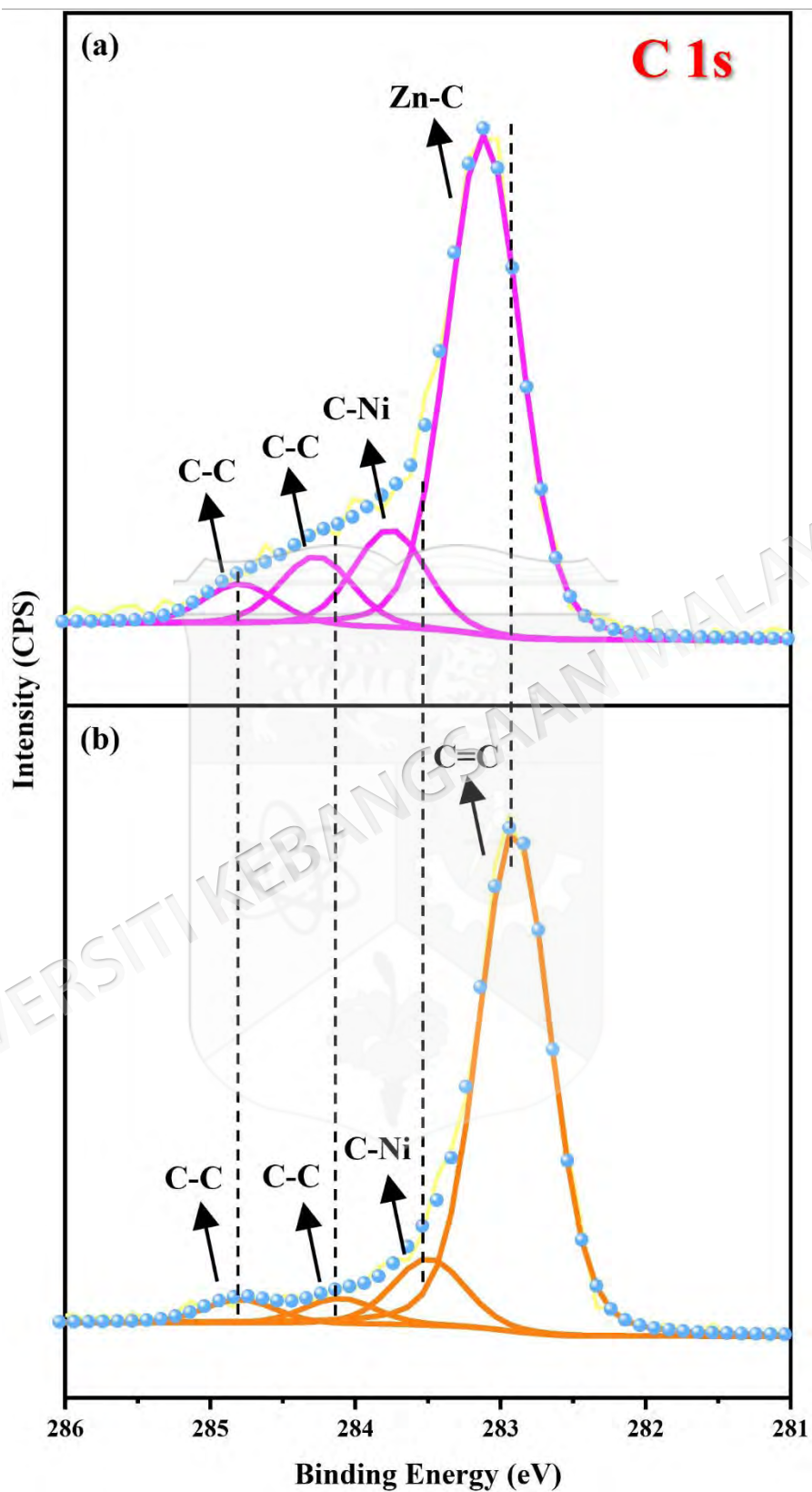


Figure 4.22 High-resolution C 1s XPS spectra of (a) ZnO/graphene/Ni-foam and (b) graphene/Ni-foam sample.

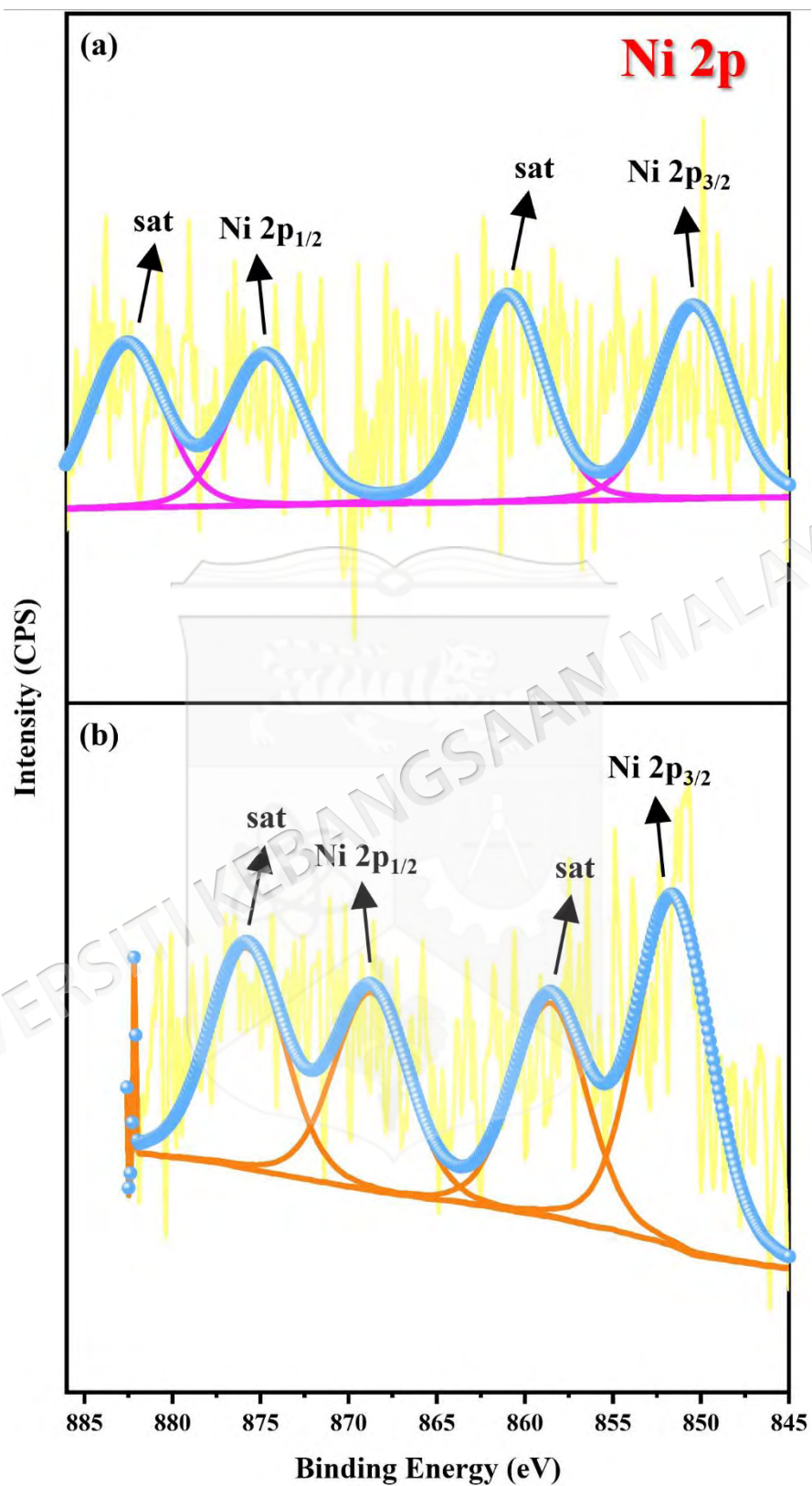


Figure 4.23 High-resolution Ni 2p XPS spectra of (a) ZnO/graphene/Ni-foam and (b) graphene/Ni-foam sample.

Table 4.9 List of binding energy for all peaks.

Peak		Binding energy (eV)		Literature	Reference
		G/Ni-foam	ZnO/G/Ni-foam		
Zn 2p	Zn 2p _{1/2}	-	1043.68	1044.30	(Shakil et al. 2018)
	Zn 2p _{3/2}	-	1020.63	1021.30	(Shakil et al. 2018)
O 1s	Zn-O	-	530.10	532.10	(Mohamed et al. 2019)
	C-O	-	525.01	528.30	(Shakil et al. 2018)
C 1s	C-C	284.80	284.82	284.80	(Mohamed et al. 2019)
	C-C	284.10	284.28	284.60	(Gao et al. 2016)
	C-Ni	283.52	283.77	283.40	(Yang et al. 2020)
	C=C	282.92	-	284.60	(Gao et al. 2016)
	Zn-C	-	283.12	282.00	(Kim & Kim 2015)
Ni 2p	Ni 2p _{1/2}	868.88	874.70	873.01	(Pal et al. 2015)
	Ni 2p _{3/2}	851.70	882.63	855.51	(Pal et al. 2015)

The PEC performance of the optimized ZnO/graphene/Ni-foam was evaluated and compared with the graphene/Ni-foam and Ni-foam samples to examine the improvement in PEC performance at each stage of modification. As illustrated in Figure 4.24 (a), a significant increase in photocurrent density was observed. Under simulated solar illumination, the Ni-foam and graphene/Ni-foam exhibited photocurrent densities of 2.81 mA/cm² and 6.75 mA/cm², respectively, at 1.23 V vs RHE. In contrast, the incorporation of the ZnO nanorod onto graphene/Ni-foam led to higher PEC performance, achieving a photocurrent density of 29.04 mA/cm² at 1.23 V vs RHE. Remarkably, this result represents a 10.33-fold increase in photocurrent density compared to the Ni-foam, and 4.30-fold enhancements over the graphene/Ni-foam.

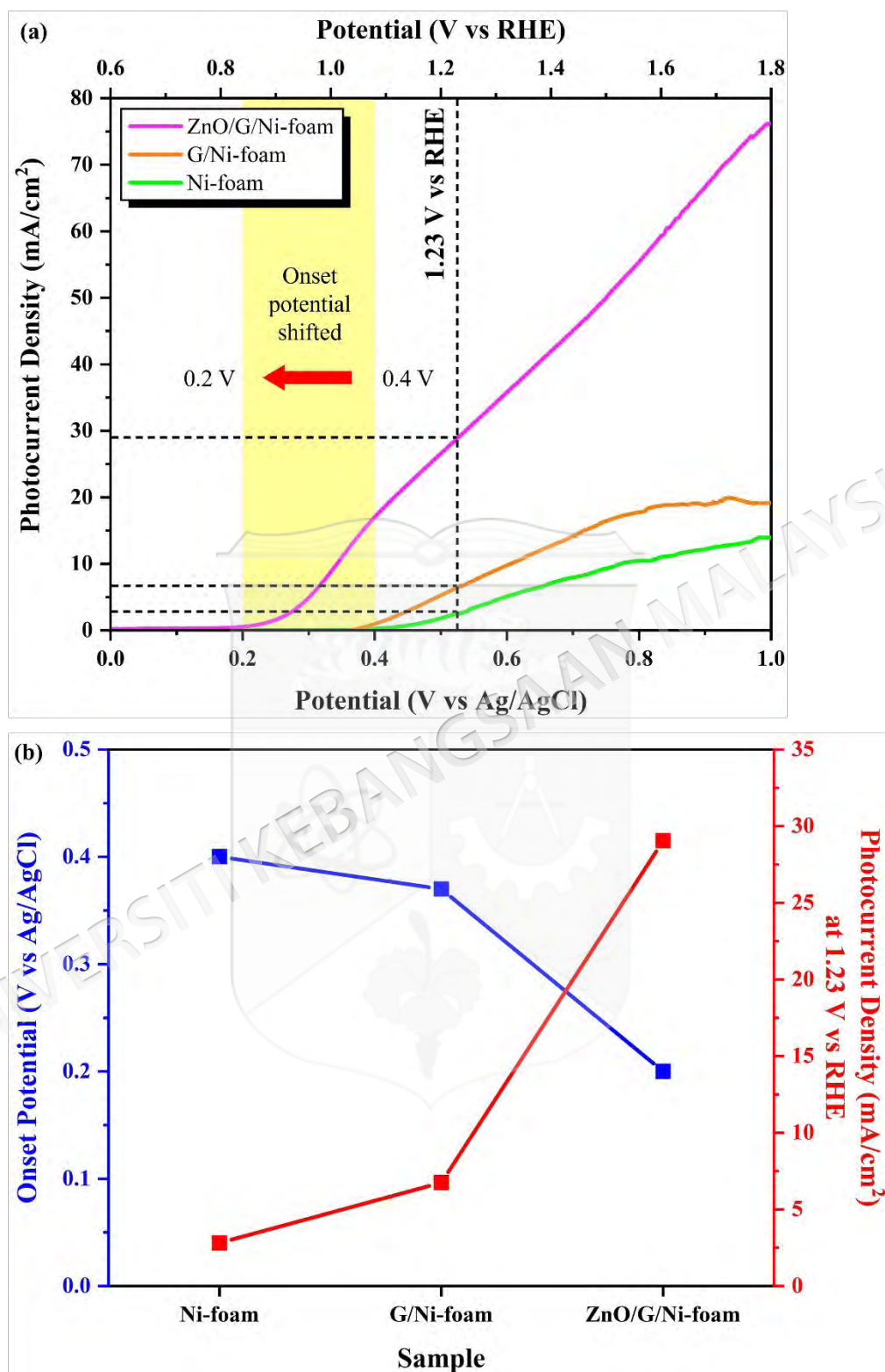


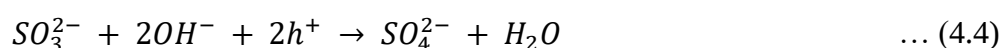
Figure 4.24 (a) LSV curves of Ni-foam, graphene/Ni-foam, and ZnO/graphene/Ni-foam measured in 0.50 M Na₂SO₃ electrolyte. The yellow region highlights the significant cathodic shift on onset potential from 0.40 V to 0.20 V vs Ag/AgCl. (b) Comparison of the corresponding onset potentials and photocurrent density for all samples.

Furthermore, a significant improvement in the onset potential was observed (Figure 4.24 (b)). While the onset potential of the Ni-foam was approximately 0.40 V vs Ag/AgCl, the onset potential for ZnO/graphene/Ni-foam shifted to 0.20 V vs Ag/AgCl. This 0.20 V shift is highly significant, as it demonstrates that the ZnO/graphene/Ni-foam structure effectively reduces the overpotential required to initiate the water oxidation reaction, allowing the PEC reaction to start at a significantly lower external bias. This improvement is attributed to the synergistic effect of the combination of ZnO, graphene, and Ni-foam architecture. The 1D hexagonal ZnO nanorods provide a higher surface area for maximized photon absorption and $e^- - h^+$ pair generation. Besides, the graphene layer serves as a high-conductive bridge (Phuan et al. 2017). This is supported by the Zn-C and Ni-C bonds identified via XPS, which confirm an intimate chemical contact that facilitates rapid electron transfer from the ZnO CB to the Ni-foam. This pathway significantly suppresses the recombination of photogenerated $e^- - h^+$ pairs, leading to an excellent PEC performance of the ZnO/graphene/Ni-foam. Moreover, the 1D ZnO nanorods morphology, combined with the high conductivity of the graphene and porous structure of the Ni-foam, facilitates deep electrolyte pathway and effective electron transport, ensuring maximum utilization of the surface area.

In addition to these structural advantages, the PEC measurements were conducted in 0.5 M Na_2SO_3 electrolyte, which serves as an efficient hole scavenger. As mentioned in Section 2.2.2b, the OER is typically become the bottleneck in PEC systems due to its kinetics sluggish four-electron transfer process (Guo et al. 2018):



By introducing SO_3^{2-} ions, the photogenerated holes reaching the ZnO surface are rapidly consumed by a simple two-electron oxidation process (Guo et al. 2018):



This electrolyte effectively suppresses $e^- - h^+$ recombination because SO_3^{2-} is oxidized much faster than H_2O molecules. Hence, it effectively extracts the hole from the ZnO

surface before it recombines with electron (Guo et al. 2018). This is validated by the onset potential of 0.20 V vs Ag/AgCl, which is assisted by this rapid hole consumption. The hole scavenger reduces the overpotential required at the photoelectrode–electrolyte interface, further highlighting the exceptional interfacial quality of the ZnO/graphene/Ni-foam.

In addition, the ABPE was utilized to evaluate the influence of incident light illumination under an applied bias, consistent with the conditions of the PEC analysis. The ABPE values were calculated using Equation (3.3). As shown in Figure 4.25, Ni-foam and graphene/Ni-foam exhibited very low efficiencies of approximately 0.01% and 0.04% at around 0.40 V vs Ag/AgCl, respectively, across the entire potential range. In contrast, the ZnO/graphene/Ni-foam achieved a significantly higher peak ABPE efficiency of 1.01% at a low applied potential of 0.35 V vs Ag/AgCl. The superior ABPE of the ZnO/graphene/Ni-foam sample is attributed to the cathodic shift in the onset potential at 0.20 V vs Ag/AgCl. Since ABPE is inversely proportional to the applied bias, the ability of the electrode to generate high photocurrent at a lower potential significantly enhances the overall conversion efficiency (Fareza et al. 2022; Rosman et al. 2025). Also, this result is contributed by the synergistic interaction between the 1D ZnO nanorods and the high conductivity bridge of graphene, which reduces the internal R_{ct} and suppresses surface recombination. Furthermore, the rapid hole consumption by the Na_2SO_3 electrolyte facilitates the high ABPE values by ensuring that the photogenerated holes are utilized efficiently at the interface before recombination can occur. These results demonstrate that the ZnO/graphene/Ni-foam effectively utilizes solar energy with minimal external electrical input, making it a promising candidate for efficient PEC water splitting.

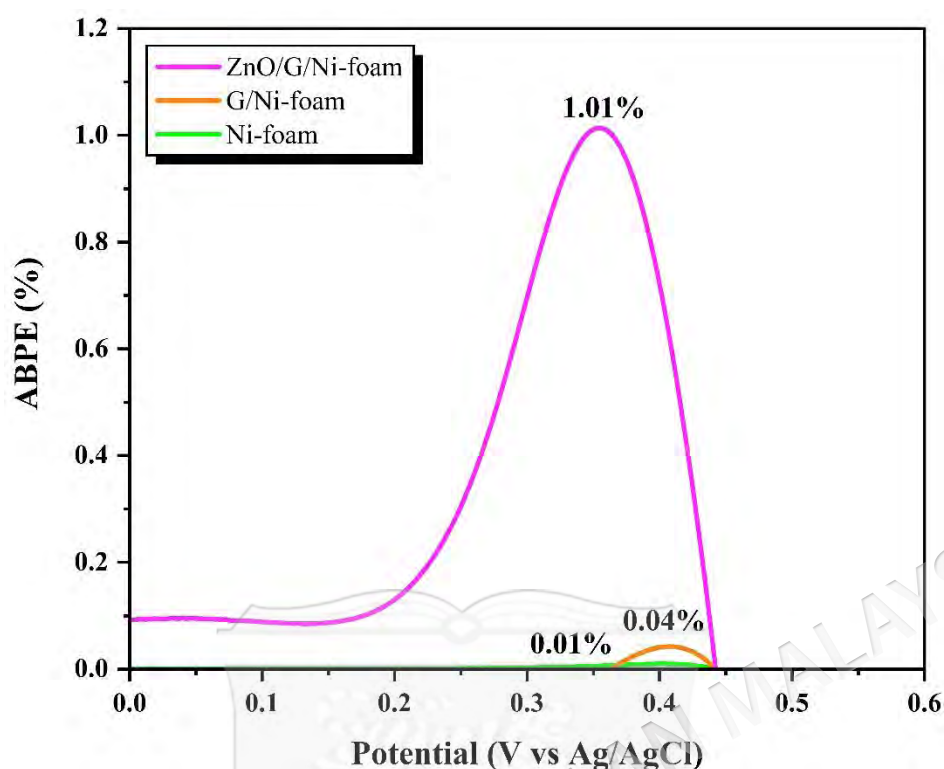


Figure 4.25 ABPE plots for Ni-foam, graphene/Ni-foam, and ZnO/graphene/Ni-foam.

EIS measurements were conducted in dark condition at 0.40 V vs Ag/AgCl to further investigate the charge transport kinetics and R_{ct} of the synthesized samples. As observed from the Nyquist plots shown in Figure 4.26, the ZnO/graphene/Ni-foam photoelectrode displays the smallest semicircle diameter, indicating the lowest R_{ct} among all tested samples. This significant reduction in resistance confirms that the combination of these three materials successfully facilitates the rapid transfer of photogenerated $e^- - h^+$ pairs. Interestingly, the discrepancy was observed between LSV and EIS results for the graphene/Ni-foam and Ni-foam samples. While the graphene/Ni-foam exhibited a higher photocurrent density compared to Ni-foam, its EIS semicircle is larger, indicating a higher R_{ct} . This contradiction can be explained by the different roles of intrinsic conductivity and photoactive behaviour.

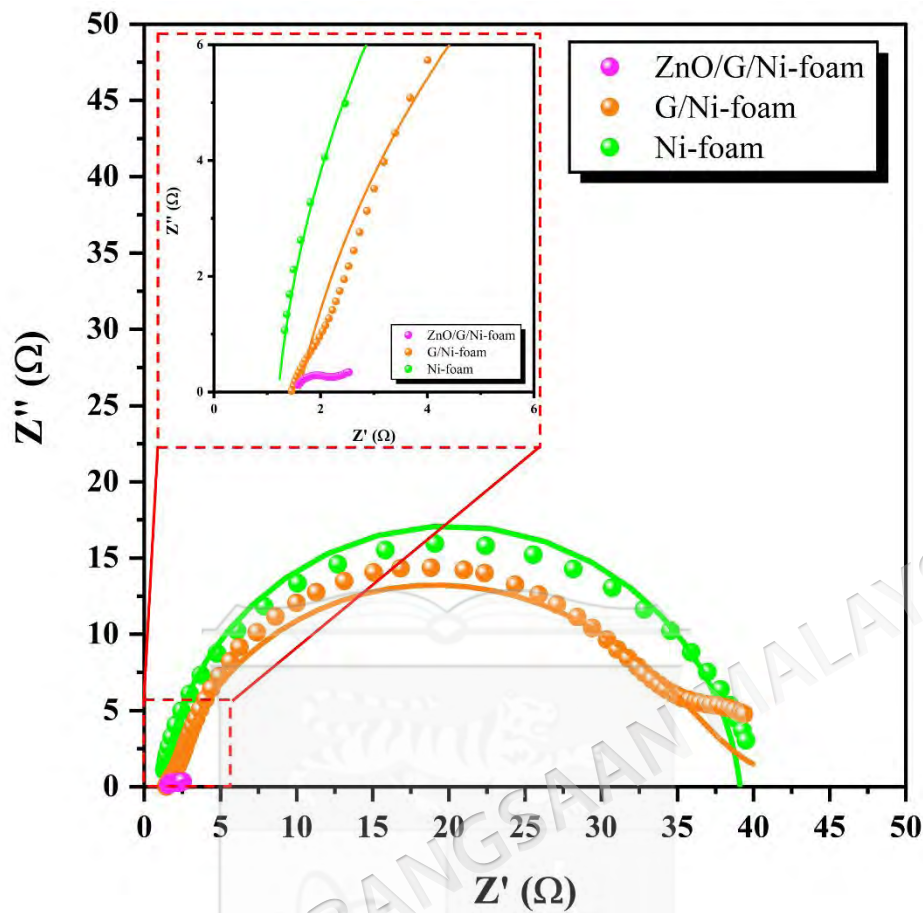


Figure 4.26 Nyquist plots for the Ni-foam, graphene/Ni-foam, and ZnO/graphene/Ni-foam with the inset for the high frequency region.

Ni-foam is a pure metallic substrate, naturally high electrical conductivity, which results in a low R_{ct} . The addition of graphene may introduce an interfacial contact resistance between the graphene layers and the Ni-foam, or between the graphene and the electrolyte, as observed in the FESEM images (Figure 4.4), where the Ni-foam was not uniformly coated by the graphene, creating gaps that hinder smooth charge flow. Furthermore, the XRD analysis confirmed the presence of NiO on the surface (Figure 4.16). The formation of NiO at the interface can introduce additional resistance compared to the pure metallic Ni surface (Grdeń et al. 2012; Nordin et al. 2025). Despite the higher R_{ct} , graphene/Ni-foam shows superior photocurrent density compared to Ni-foam because graphene provides more active sites and excellent electronic characteristic for charge separation under light conditions than Ni-foam.

To further elucidate the electronic properties and charge carrier dynamics of the photoelectrode, Mott-Schottky measurements were performed. The Mott-Schottky plots for the Ni-foam, graphene/Ni-foam, and ZnO/graphene/Ni-foam are presented in Figure 4.27. All samples exhibited a positive slope, confirming the n-type semiconductor nature, called as photoanode, where electron are the majority charge carriers (Anuar et al. 2025). The N_d was calculated from the slope of the linear region using Equation (3.5). The results show that the ZnO/graphene/Ni-foam achieved higher N_d of $1.17 \times 10^{20} \text{ cm}^{-3}$ compared to graphene/Ni-foam ($1.78 \times 10^{19} \text{ cm}^{-3}$) and Ni-foam ($2.41 \times 10^{19} \text{ cm}^{-3}$). This increase in N_d is attributed to the presence of graphene layer as a conductive bridge that facilitates the efficient injection of electron from the ZnO to the Ni-foam substrate, which effectively increasing the available carriers for the PEC water splitting reaction. Furthermore, the higher N_d observed in the Mott-Schottky analysis is highly consistent with the reduced R_{ct} observed in EIS and the superior photocurrent density achieved in LSV measurements.

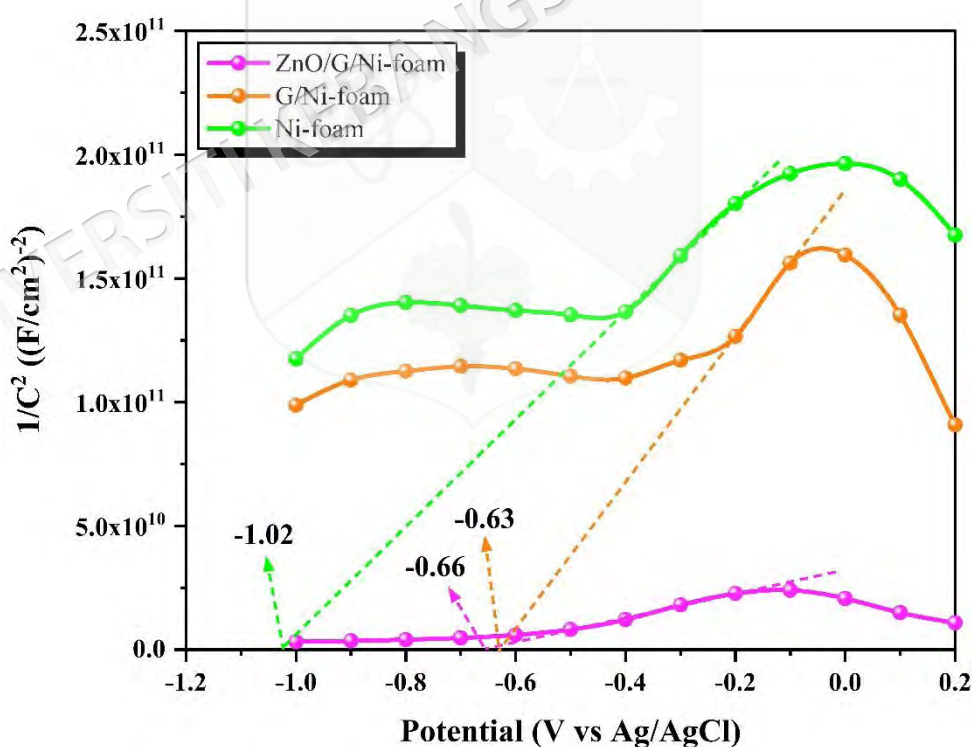
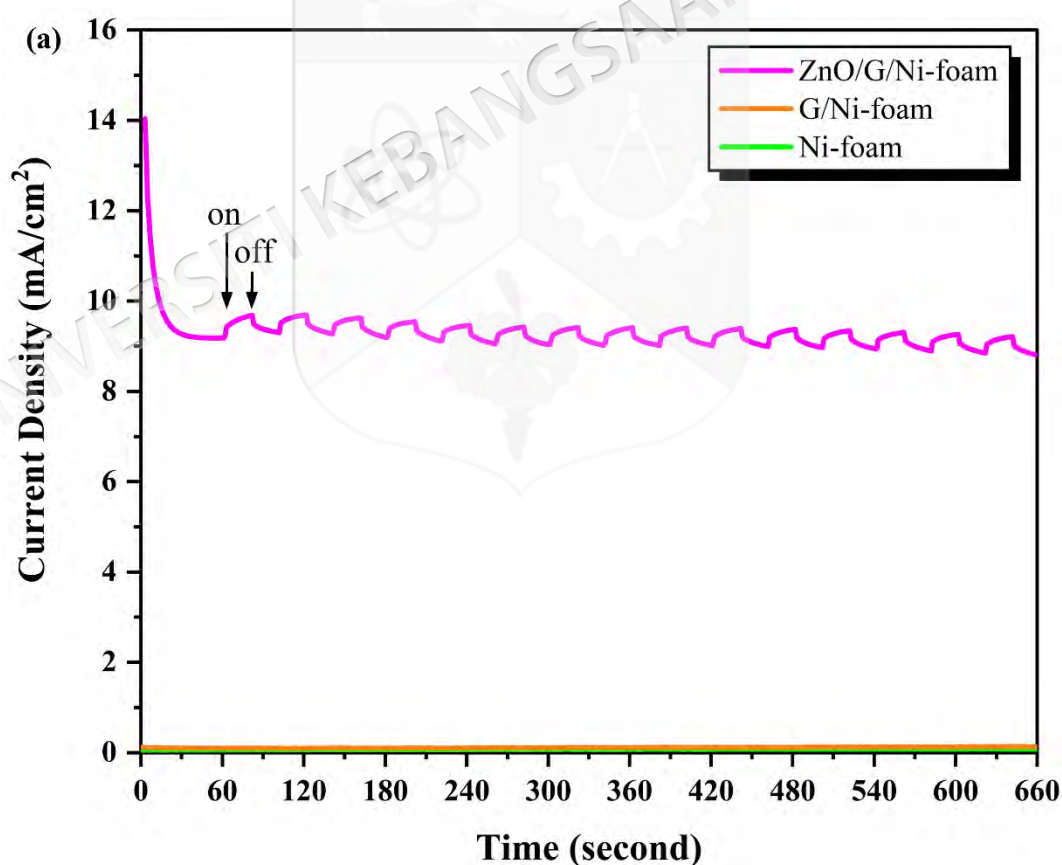


Figure 4.27 Mott-Schottky plot for Ni-foam, graphene/Ni-foam, and ZnO/graphene/Ni-foam.

Next, the transient photocurrent response of the samples was evaluated under chopped illumination at 0.40 V vs Ag/AgCl, as shown in Figure 4.28 (a). The ZnO/graphene/Ni-foam sample showed a photoactive behaviour, explained by a complex response by an instantaneous photocurrent jump followed by a gradual rise to a steady state (a “hill-like” shape). The initial vertical jump indicates the rapid separation and transport of photogenerated $e^- - h^+$ pairs. The subsequent gradual rise, or “hill” shape, is attributed to trap-mediated electron and the filling of surface states defects. Then, the slight downward trend after the light of switch off shows that the photocurrent over successive cycles. In contrast, the Ni-foam and graphene/Ni-foam samples displayed negligible photocurrent under the same conditions. It confirmed that these samples do not really contribute to the PEC activity as it does not consist of photoactive material (Khan et al. 2018).



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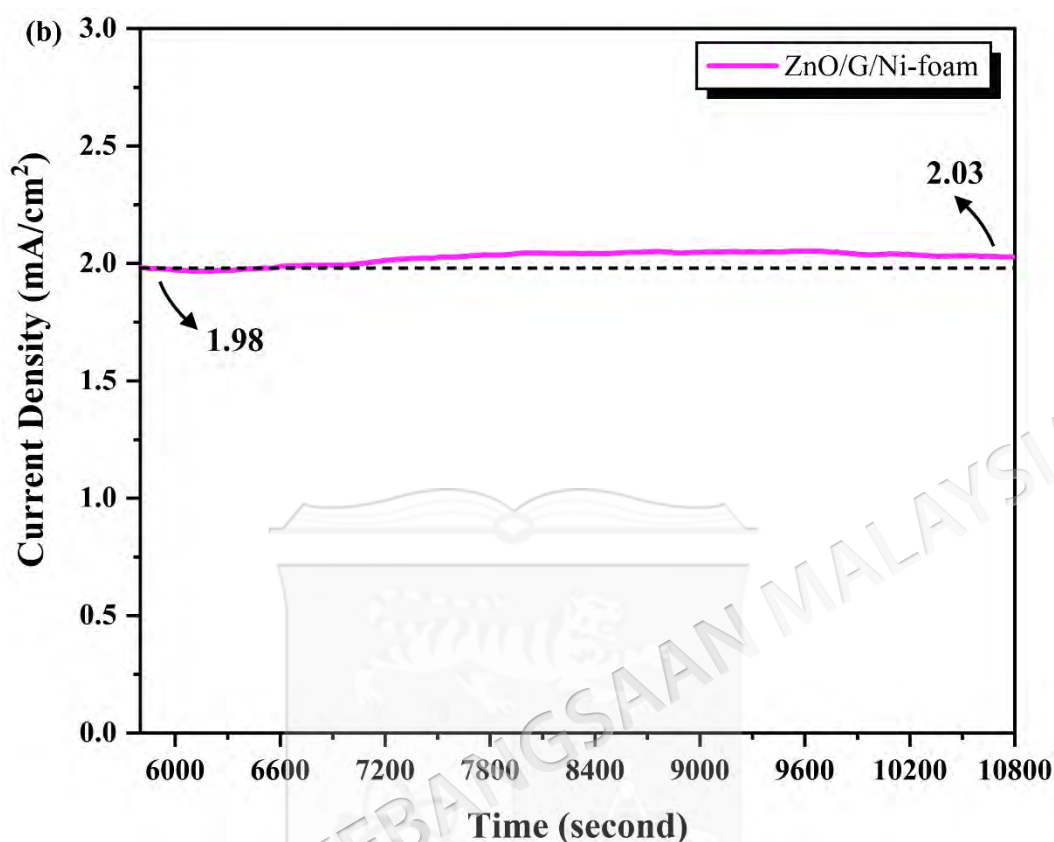


Figure 4.28 (a) Photocurrent response (chopped-light curves) of Ni-foam, graphene/Ni-foam, and ZnO/graphene/Ni-foam at 20-second intervals and (b) Stability test of ZnO/graphene/Ni-foam photoanode over 3 hours under continuous illumination.

The stability of the ZnO/graphene/Ni-foam photoanode was evaluated via CA at a constant potential of 0.40 V vs Ag/AgCl for 3 hours under continuous illumination. As shown in Figure 4.28 (b), the current density is presented from the point of stabilization to exclude the initial transient photocurrent spikes or drops and the saturation of surface trap states during the formation of the interface between the photoelectrode and the electrolyte (Li et al. 2021). This approach allows for a more accurate assessment of the material's resistance to photocorrosion. The ZnO/graphene/Ni-foam photoanode demonstrates remarkable durability, maintaining its performance throughout the 3 hours. Interestingly, the current density exhibited a slight upward trend, increasing from 1.98 mA/cm² to 2.03 mA/cm², suggesting a gradual activation of the photoanode surface. Due to the highly porous structure of the Ni-foam, this trend is likely attributed to the time required for the electrolyte to

uniformly access the 3D framework and contact all available active surfaces for the water splitting reaction. While minor fluctuations in current may occur, this common behaviour often appearing concurrently with specific voltage behaviours during prolonged reaction (Li et al. 2021).

During the reaction, photogenerated electron are efficiently transferred to the Pt to drive the HER, while photogenerated holes migrate to the surface to participate in the OER (Nasr et al. 2022). Furthermore, the presence of graphene layer and the Na_2SO_3 hole scavenger play a synergistic role in enhancing stability. Graphene facilitates rapid charge separation, preventing the accumulation of hole at the ZnO surface, while the hole scavenger effectively consumes hole at the surface, thereby significantly suppressing the photocorrosion of the ZnO. Despite the minor degradation, the stability of the ZnO/graphene/Ni-foam remains outstanding. This confirms that the incorporation of these three materials not only improve photoactivity but also provides a robust structure for sustained H_2 production under illumination.

To further understand the slight increment in current density observed after 3 hours of stability test, post-characterization by FESEM and XRD analyses were conducted on the ZnO/graphene/Ni-foam photoanode. FESEM images in Figure 4.29 (a-d) revealed that the graphene layer remained coated on the Ni-foam surface, showing only slight degradation following the stability test. This robust stability is directly attributed to the strong interfacial adhesion and high adsorption energy at the graphene/Ni-foam interface (Christian et al. 2017; Gadisa et al. 2019; Hamada & Otani 2010; Xu & Buehler 2010).

While for the ZnO, two different morphological regions, indicating a non-uniform degradation process across the ZnO/graphene/Ni-foam photoanode (Figure 4.29 (e, f)). The 1D nanorod morphology was largely preserved in certain regions. However, the hexagonal facets exhibited clear evidence of etching and a flaky morphology, resulting from the slow dissolution of Zn^{2+} ions into the electrolyte (Figure 4.29 (f) (i)). In other impacted areas (Figure 4.29 (f) (ii)), the ZnO nanorods show significant structural transformation, turns into debris and cluttered aggregates. This non-uniform degradation suggests that while the graphene layer provides a stable

electronic foundation, the ZnO remains susceptible to localized photocorrosion. Interestingly, this morphological reconstruction likely increases the active surface area, which explains the slight increase in current density observed toward the end of the stability test.

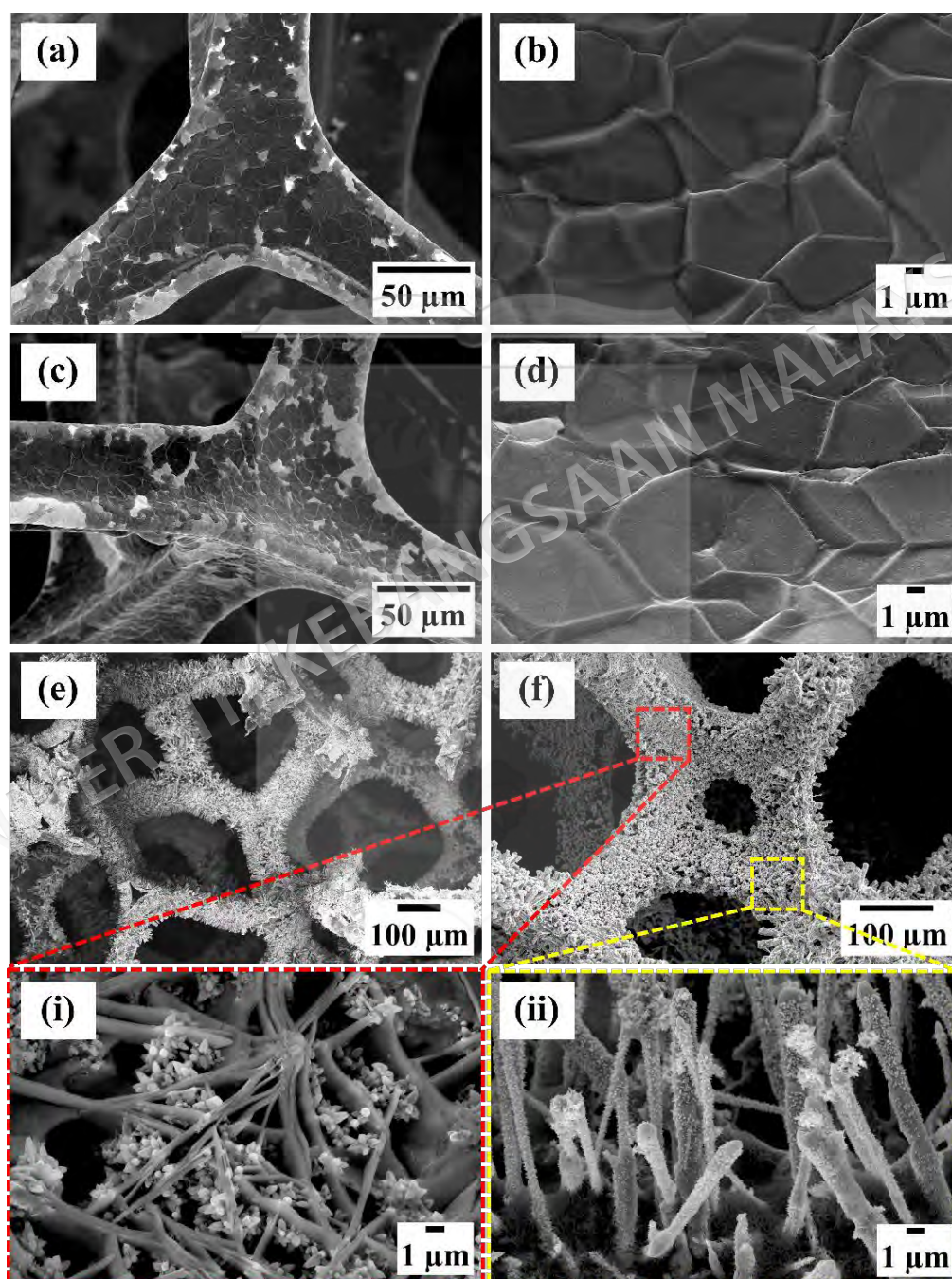


Figure 4.29 FESEM images at low (500x) and high (5,000x) magnifications of graphene/Ni-foam (a, b) before and (c, d) after stability testing, as well as ZnO/graphene/Ni-foam (e) before and (f) after stability testing. The insets show the transformation of ZnO morphology into (i) flaky and (ii) debris-like structures.

XRD characterization of the ZnO/graphene/Ni-foam after the 3-hour stability test confirms that all characteristic diffraction peaks for carbon, ZnO, and Ni remain the same, indicating that the fundamental phases remained intact (Xu et al. 2024). However, a distinct shift (less than 1°) was observed across all diffraction peaks for ZnO/graphene/Ni-foam after PEC testing (Figure 4.30). This shift indicates the presences of lattice strain induced by the operating conditions of the PEC reaction, especially the continuous applied bias, prolonged light irradiation, and the interaction of ions from the electrolyte. This structural distortion, together with the morphological evolution from well-defined hexagonal rods to flaky and debris aggregates, contributes to an increased active surface area and modified electronic and interface properties of the ZnO/graphene/Ni-foam. These factors enhance the charge transfer across the ZnO/graphene/Ni-foam interface, significantly boosting the photoactivity of the photoanode.

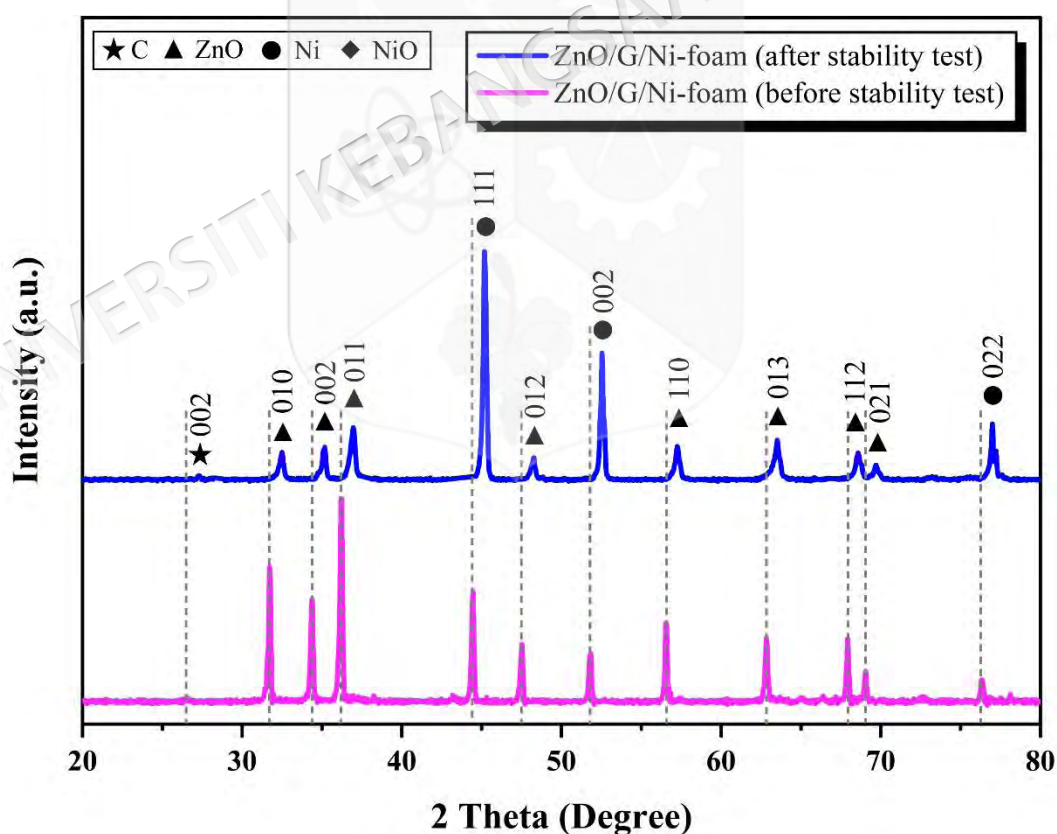


Figure 4.30 Comparison of XRD pattern for the ZnO/graphene/Ni-foam.

4.6 HYDROGEN PRODUCTION

The solar-to-hydrogen (STH) conversion capability of the photoelectrodes was validated by measuring the volume of evolved H_2 gas under one sun illumination. The experimental H_2 yield was compared against the theoretical yield derived from the total charge passed during the stability test. Figure 4.31 shows the cumulative H_2 production in 1 hour at an applied potential of 0.40 V vs Ag/AgCl. The result clearly indicates that the ZnO/graphene/Ni-foam photoanode achieved the highest H_2 evolution rate of 1.72 mL/hour, significantly outperforming the control samples. This performance is higher than reported ZnO nanorods by Chia et al. (2025), around 5.54×10^{-3} mL/hour. Interestingly, the graphene/Ni-foam produced 1.20 mL/hour, and this value was lower than the Ni-foam (1.44 mL/hour). This observation aligns with the EIS results (Figure 4.26). Although the presence of graphene enhances photocurrent density (Figure 4.24), the R_{ct} is higher caused by not fully coated graphene and the presence of NiO, which can be seen in FESEM (Figure 4.11 (c)) and XRD analysis (Figure 4.16). This behavior limits the efficient electron transport required to sustain the H_2 gas evolution.

Consequently, the Faraday Efficiency (FE) analysis focused on the best performing sample, which is ZnO/graphene/Ni-foam photoanode, to evaluate its charge-to-fuel and STH conversion performance, using Equations (3.6), (3.7), (3.8) and (3.9) (as detailed in Appendix B). The ZnO/graphene/Ni-foam photoanode achieved a high FE of 90.92% and an STH efficiency of 2.81% at 1.08 V vs RHE (0.40 V vs Ag/AgCl). This high efficiency is attributed to the synergistic effects of the integration of ZnO, graphene, and Ni-foam. Each of the materials play an important role, where (i) 1D ZnO nanorods provide a high surface area and a direct pathway for charge carrier transport, (ii) graphene interlayer acts as a high-conductivity bridge, facilitating rapid electron separation and transfer to the Ni-foam substrate, and (iii) porous Ni-foam offers a robust 3D framework that maximizes active sites and facilitates electrolyte flow and bubble release during the PEC reaction. By reducing internal resistance, the graphene interlayer ensures that photogenerated $e^- - h^+$ are effectively utilized for H_2 production rather than being lost to recombination.

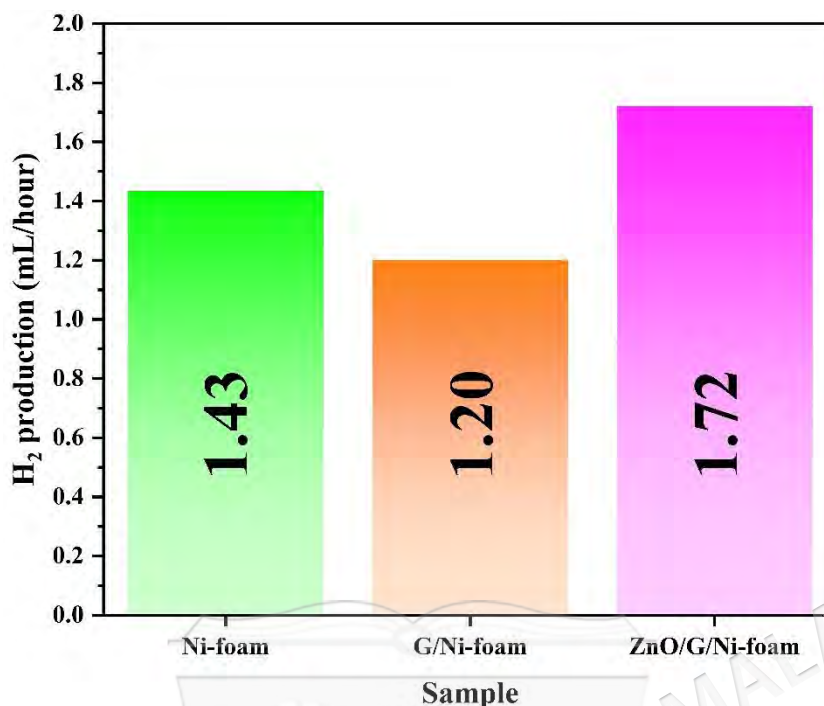


Figure 4.31 Cumulative H₂ gas production under 1 hour of illumination.

However, a minor efficiency loss from the FE was observed. As previously confirmed by post-PEC FESEM morphology, this loss is due to photocorrosion of the ZnO nanorods. The observed surface etching and debris formation indicate that some of the photogenerated holes, not reacting with the Na₂SO₃ electrolyte, contributed to the slow dissolution of the ZnO. Nevertheless, the results confirm that the ZnO/graphene/Ni-foam structure is highly efficient and sustainable for solar-driven water splitting.

4.7 INFLUENCE OF INTERFACE STRUCTURE ON THE PROPERTIES OF ZnO/GRAPHENE/NICKEL (111) VIA DFT

To fundamentally understand the mechanisms that determine the enhanced PEC performance of the ZnO/graphene/Ni-foam configuration, a first-principles study based on DFT was conducted. It should be noted that the simulated ZnO/graphene/Ni (111) structure serves as an idealized atomic-scale representation of the experimental ZnO/graphene/Ni-foam interface. While experimental results indicated strong interfacial interaction between ZnO, graphene, and Ni substrate, DFT allows for a precise atomistic investigation into the electronic properties of ZnO/graphene/Ni. The main objectives of this computational study are (i) to determine the most stable

configurations of ZnO/graphene/Ni, (ii) to investigate the relationship between the interfacial structure and the electronic and PEC properties, and (iii) to elucidate the charge transfer mechanisms that facilitate the high PEC performance.

Before developing the trilayer interface, the bulk properties of the individual components were optimized to ensure the accuracy of the chosen functionals and pseudopotentials. Figure 4.32 depicts the optimized geometrical structures for bulk ZnO, graphene, and Ni (111) surface. To ensure the reliability and accuracy of computational model, the calculated parameters were compared with reported experimental values, as summarized in Table 4.10. For the bulk wurtzite ZnO, the calculated lattice constants ($a = b = 3.27 \text{ \AA}$ and $c = 5.28 \text{ \AA}$) from this work, are in excellent agreement with the estimated experimental values ($a = b = 3.57 \text{ \AA}$ and $c = 5.20 \text{ \AA}$) (Karzel et al. 1996). Similarly, for graphene, the calculated lattice constant ($a = b = 2.47 \text{ \AA}$) is nearly identical to the estimated experimental value of $2.46 \text{ \AA}$ (Zheng et al. 2017). For the Ni (111) surface, the nearest neighbor distance ($d_{\text{Ni-Ni}}$) of $2.45 \text{ \AA}$ is closely matches the estimated experimental value of $2.49 \text{ \AA}$ (Shao et al. 2017). The minimum discrepancy between the calculated and experimental parameters should be less than 3% to confirms the reliability of the DFT model in describing the structural and electronic properties of the ZnO/graphene/Ni configuration (Bovgyra et al. 2020).

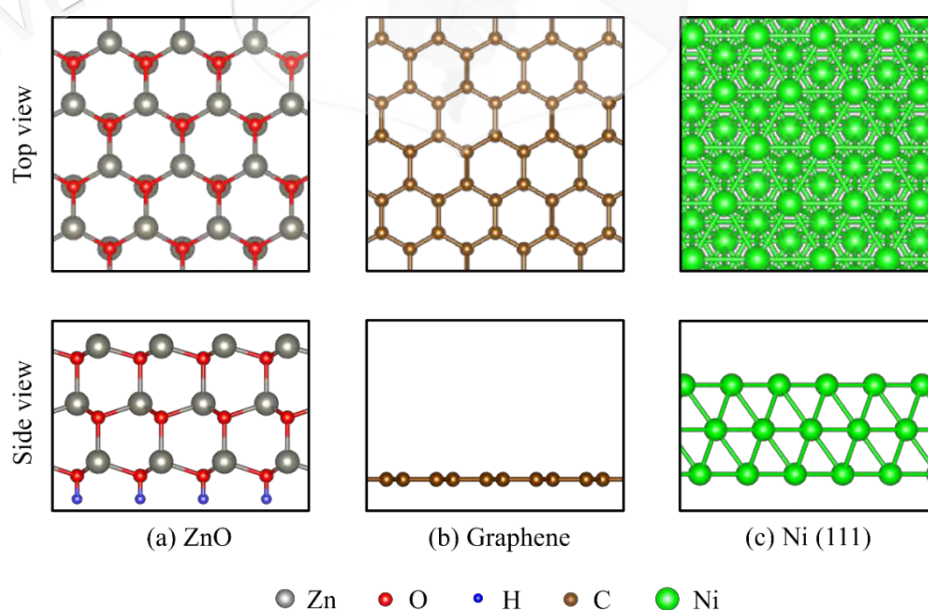


Figure 4.32 Optimized geometrical structures of (a) bulk ZnO, (b) graphene, and (c) Ni (111) surface.

Table 4.10 Comparison of optimized structural parameters with experimental values from literature.

Material	Parameter	This work (Å)	Literature (Å)	Discrepancy (%)	Reference
ZnO	Lattice constant (a = b)	3.27	3.25	0.61	(Karzel et al. 1996)
	Lattice constant (c)	5.28	5.20	1.54	
G	Lattice constant (a = b)	2.47	2.46	0.40	(Zheng et al. 2017)
Ni (111)	Nearest neighbor distance ($d_{\text{Ni-Ni}}$)	2.45	2.49	1.60	(Shao et al. 2017)

Prior to constructing the ZnO/graphene/Ni structure, the bulk structures were transformed into slab models based on the lattice constant of ZnO (Figure 4.33). As mentioned in Chapter III (Section 3.9), Ni is hard and ductile, graphene is flexible, and ZnO is a rigid material. Therefore, the supercell dimensions were carefully determined by adjusting the lattice constants of Ni and graphene to match the that of ZnO, thereby minimizing strain within the ZnO lattice.

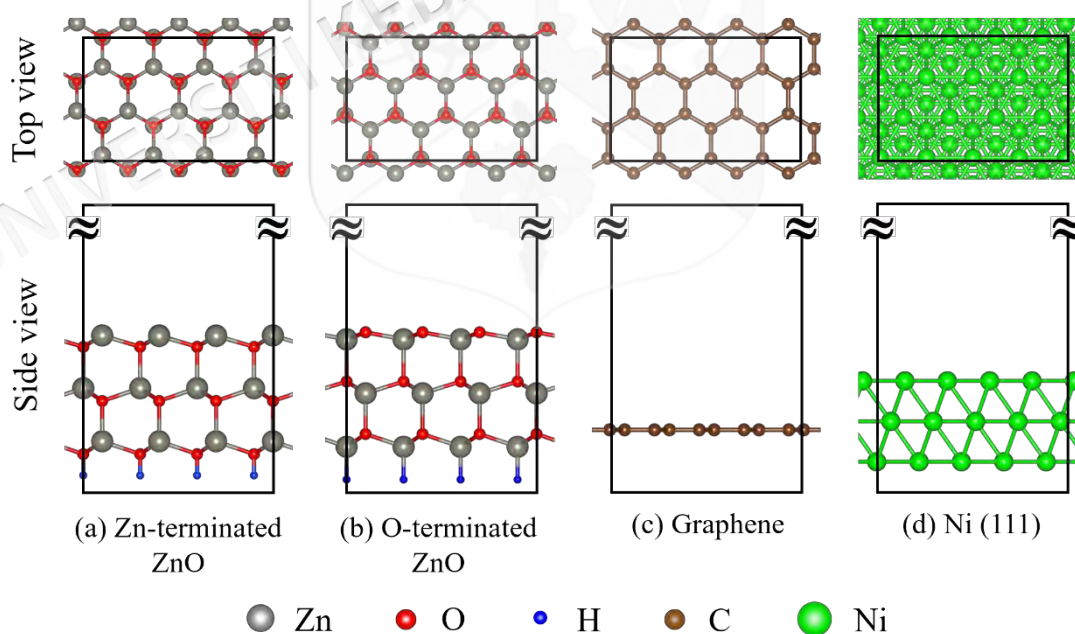


Figure 4.33 Atomic slab models of (a) Zn-terminated ZnO, (b) O-terminated ZnO, (c) graphene, and (d) Ni (111) to match the ZnO lattice parameters.

Following that, two polar slab models were constructed for ZnO/graphene: Zn-terminated (0001) surface and O-terminated surface (000 $\bar{1}$) ZnO/graphene (Figure 4.33). These models represent the most common configurations found in the 1D nanorods synthesized experimentally. The structure of both ZnO surfaces remained unchanged after relaxation with the graphene layer. However, the graphene layer exhibited a slight distortion at the interface. While no significant distortion is observed in the ZnO structures, the graphene layer undergoes localized structural rearrangement to accommodate the lattice mismatch and interfacial interaction with the ZnO. This observation is attributed to the difference in lattice parameters. Since the lattice constant of graphene is smaller than ZnO, the graphene layer must shift from their ideal planar positions to align with the ZnO supercell. This ability of graphene to accommodate epitaxial strain while maintaining its electronic properties is a main factor in the stability of the ZnO/graphene interface, ensuring the efficient charge transfer observed in the PEC measurements.

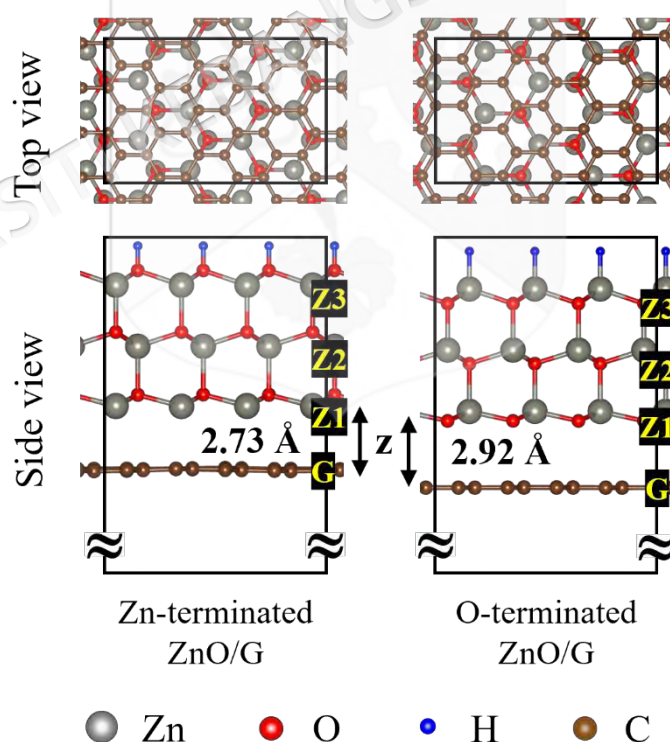


Figure 4.34 Optimized ZnO/graphene configurations for the (a) Zn-terminated and (b) O-terminated interfaces, with the calculated interfacial distances between the first layer of ZnO and graphene.

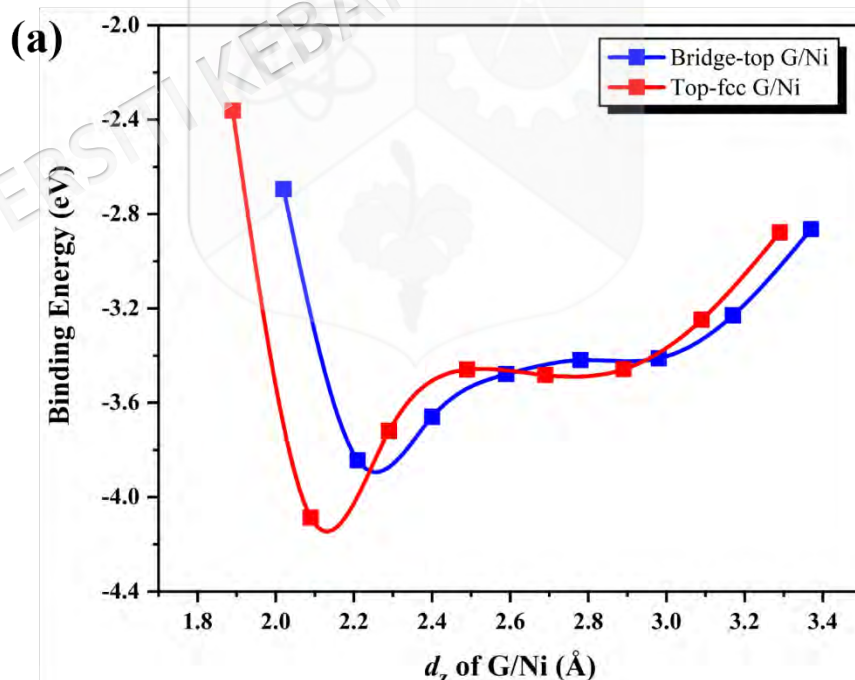
Furthermore, a clear correlation is observed between the E_b (Equation (3.10)) and the interfacial distance in z-direction (d_z). As tabulated in Table 4.11, the Zn-terminated ZnO/graphene interface exhibits a more negative E_b (-2.90 eV) compared to the O-terminated ZnO interface (-2.54 eV). This increased thermodynamic stability corresponds directly with a shorter interfacial spacing in the z-direction, where $d_z = 2.73$ Å for the Zn-terminated surface compared to $d_z = 2.92$ Å for the O-terminated surface. These results are in excellent agreement with previously reported work by Xu et al. (2013). The reduction in d_z at the Zn-terminated interface indicates enhanced orbital hybridization between the zinc atoms and the graphene layer, which strengthens the interfacial bond. Additionally, the calculated $E_{b/n}$ (-90 meV and -80 meV for the Zn- and O-terminated, respectively) suggests that vdW interactions also exist within the configuration (Geng et al. 2013). This indicates that long-range vdW forces and localized chemical hybridization work together to stabilize the ZnO/graphene heterostructure. Consequently, because the Zn-terminated ZnO/graphene configuration (denotes as ZnO/graphene) provides the most stable interface, it was selected as the primary model for interfacing with the Ni layer to construct the complete trilayer photoanode configuration.

Table 4.11 Equilibrium distances, total binding energy, and binding energy per carbon atom between ZnO/graphene configurations.

Surface termination	Interlayer distance, d_z (Å)	Binding energy, E_b (eV)	Binding energy per carbon atom, $E_{b/n}$ (meV/C)
Zn-terminated	2.73	-2.90	-90
O-terminated	2.92	-2.54	-80

Before constructing the full trilayer ZnO/graphene/Ni configuration, it was essential to determine the most stable configuration for the graphene/Ni interface. Based on reported literature in Chapter II Section 0 (b), the Bridge-top and Top-fcc configurations are the most favourable adsorption sites for graphene on a Ni (111) surface. To identify the equilibrium state, the d_z of graphene/Ni was optimized using Self-Consistent Field (SCF) calculations. The optimal d_z was determined by identifying the minimum E_b , calculated according to Equation (3.10) using the optimized geometries of isolated graphene and the clean Ni (111) substrate. The resulting E_b values are plotted in Figure 4.35 (a).

As shown in Figure 4.35, the results show that the Bridge-top configuration reaches its most stable state at a d_z of 2.21 Å with E_b of -3.90 eV. In contrast, the Top-fcc configuration exhibits a shorter d_z of 2.09 Å and a more negative $E_b = -4.11$ eV, while maintaining a nearly similar height (h) between the graphene and the bottommost Ni layer (Table 4.12). These findings are in excellent agreement with the values reported by Hamada & Otani (2010). This shorter distance in the Top-fcc configuration facilitates stronger orbital hybridization between the Ni 3d states and the graphene π -orbitals, make the interaction between Ni and graphene become stronger, with chemisorption energy minimum (Christian et al. 2017; Hamada & Otani 2010). This behaviour is advantageous for reducing interfacial charge resistance. Hence, the Top-fcc graphene/Ni configuration was selected for layering with the Zn-terminated ZnO slab. By combining these two most optimized interfacial models: Zn-terminated ZnO/graphene (ZnO/graphene) and Top-fcc graphene/Ni (graphene/Ni), an optimized trilayer ZnO/graphene/Ni configuration was validated for subsequent charge transfer analysis.



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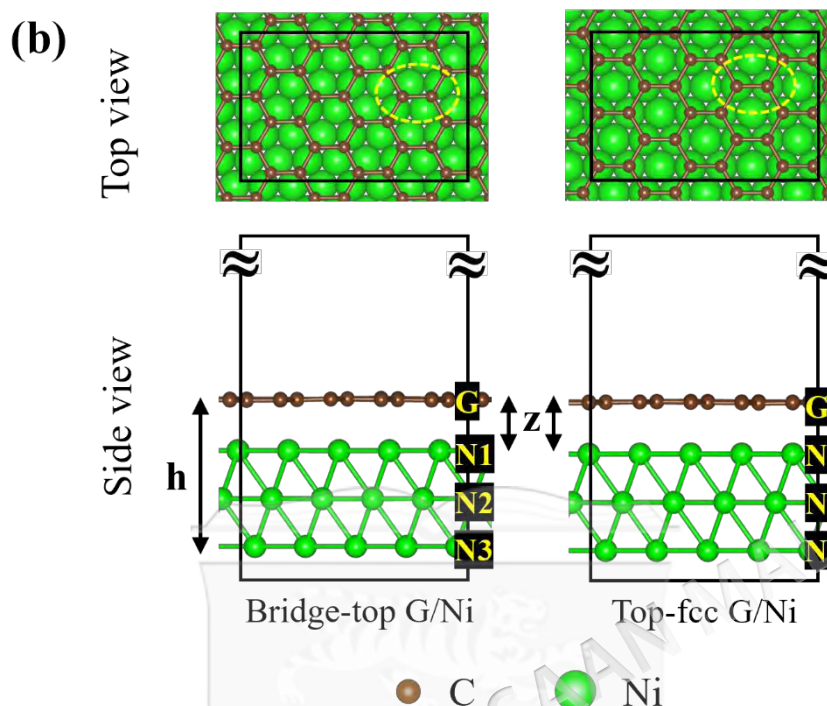


Figure 4.35 (a) Binding energy for two configurations of graphene/Ni. (b) Relax atomic structure of the Bridge-top graphene/Ni and Top-fcc graphene/Ni, with equilibrium distances. The yellow circles indicate the position of the graphene on the Bridge and Top sites on the Ni surface.

Table 4.12 Equilibrium interlayer distances, total binding energy, and binding energy per carbon atom for the graphene/Ni configurations.

Adsorption site	Interlayer distance, d_z (Å)	Binding energy, E_b (eV)	Binding energy per carbon atom, $E_{b/n}$ (meV/C)
Bridge-top	2.21	-3.90	-122
Top-fcc	2.09	-4.11	-128

As shown in Figure 4.36, the three components configuration was constructed by sandwiching the graphene layer between the Zn-terminated ZnO (0001) surface and the Top-fcc Ni (111) substrate, like the experimental setup. To determine the equilibrium state of the ZnO/graphene/Ni, the total energy of the configuration was calculated by varying the h between the first layer of ZnO and the bottommost Ni layer in the z -direction. The trilayer configuration achieved its most stable configuration at an optimized h of 8.78 Å, where the distance between the first layer of ZnO and the graphene layer (z_1) is 2.58 Å and the distance between the graphene layer and the

topmost Ni layer (z_2) is 2.21 Å. The resulting E_b for the ZnO/graphene/Ni was -9.26 eV, which is significantly more negative than the bilayer ZnO/graphene and graphene/Ni configurations. The summary of optimized parameters is tabulated in Table 4.13.

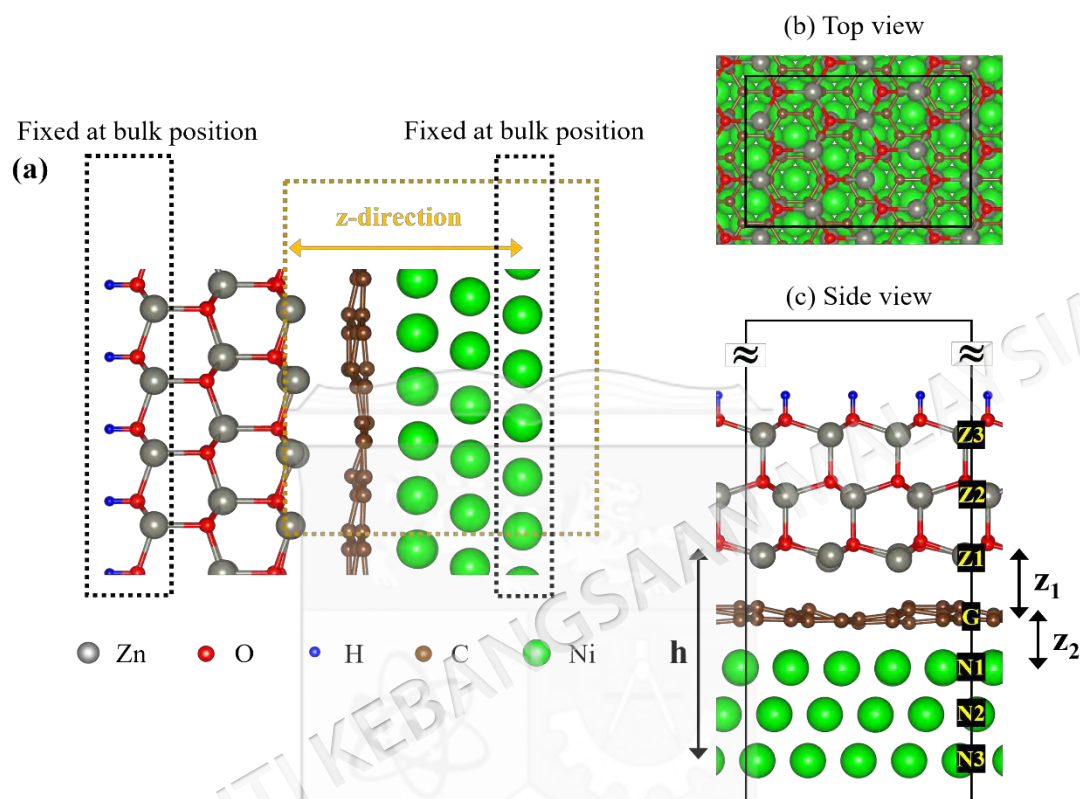


Figure 4.36 (a) Schematic diagram illustrating the height adjustment between the first layer of ZnO and the bottommost layer of Ni. The optimized Zn-terminated ZnO/Top-fcc graphene/Ni interface from the (b) top and (c) side views.

Table 4.13 Structural parameters of the optimized trilayer configuration.

Parameter	Optimized value (Å)	Description
Total height at z-direction (h)	8.78	Height between the first layer of ZnO and the bottommost Ni layer
ZnO/graphene (z_1)	2.58	Interfacial distance between the first layer of ZnO and the graphene layer
Graphene/Ni (z_2)	2.21	Interfacial distance between the graphene layer and the first layer of Ni

Upon achieving the fully relaxed equilibrium state of the ZnO/graphene/Ni configuration, a noticeable structural distortion was observed at the interfaces. Specifically, atoms in the first layers of ZnO shifted toward the graphene layer to

maximize orbital overlap. This movement resulted in an elongation of the interfacial Zn-O bond lengths, driven by the strong chemical attraction between the Zn 3d orbitals and the graphene π -systems (Liu et al. 2019). The Zn atoms are pulled toward the graphene, indicating that the interfacial binding force is strong enough to slightly deform the local wurtzite lattice. Simultaneously, the graphene layer exhibited a significant distortion (0.50 Å). Instead of maintaining a flat surface, the carbon atoms tend to move towards the zinc atoms, suggesting a strong bonding interaction exists between carbon and the ZnO interface, which can be used to indicate that the Zn-C bond, as can be seen in XPS result (Figure 4.22).

These distortions are beneficial to the performance of the photoanode. This is because, the elongation of the Zn-O bond and the reduction in the Zn-C distance facilitate a stronger interfacial interaction and superior electronic coupling, as discussed in the previous paragraph. This configuration reduces the physical barrier for photogenerated electrons to move from ZnO nanorods into the graphene conductive bridge before reaching the Ni surface. Furthermore, these results demonstrate that the trilayer configuration possesses enhanced stability compared to the bilayer configurations, as evidenced by the calculated E_b and E_{int} values, using Equation (3.10) and (3.12), illustrated in Figure 4.37. This is attributed to a synergistic effect where the graphene interlayer acts as a conductive bridge, effectively bridging the semiconductor ZnO and the metallic Ni.

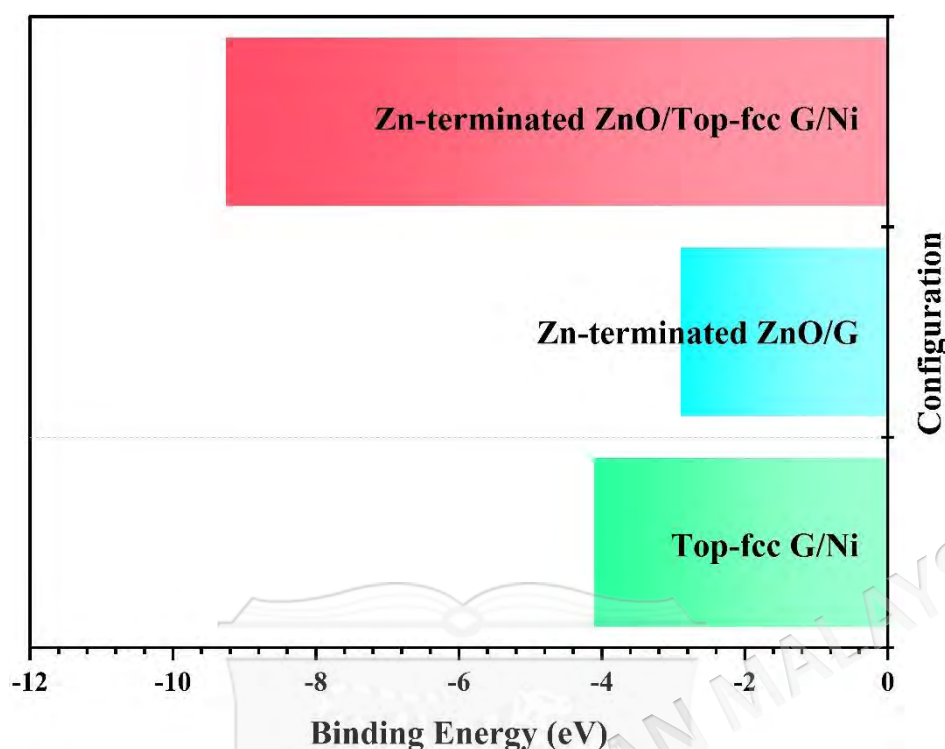


Figure 4.37 Comparative analysis of the binding energy between bilayer and trilayer configurations.

In addition, these result shows that the interfacial strength of the isolated bilayer configurations is primarily governed by vdW interactions, while the short-range chemical interactions exhibit a repulsive character, as calculated using Equation (3.11). Although the vdW interactions remains a crucial role in the ZnO/graphene/Ni interface, the short-range chemical interactions become attractive. This indicates that the chemical effects contribute significantly to the overall stabilization of the ternary configuration, as summarized in Table 4.14. As a result, the d_z are reduced, leading to a physical modification of the graphene layer. Specifically, the hexagonal six-membered carbon rings in graphene layer become distorted, enhancing the electronic properties and chemical bonding between the ZnO and the Ni mediated by the graphene bridge. These DFT findings provide a theoretical basis that directly supports the enhanced photocurrent density observed in the experimental results.

Table 4.14 Calculated binding energy and interaction energy for the bilayer and trilayer configurations.

Configuration	E_b (eV)	E_b^{vdW} (eV)	E_{int} (eV)	E_{int}^{vdW} (eV)	Contribution from vdW (%)	Contribution from chemical interaction (%)
ZnO/graphene (Bilayer)	-2.90	-3.01	N/A	N/A	103.67	-3.66
Graphene/Ni (Bilayer)	-4.11	-5.95	N/A	N/A	144.70	-44.70
ZnO/graphene/Ni (Trilayer)	-9.26	-9.99	-2.25	-1.03	45.87	54.13

4.8 CHARGE TRANSFER MECHANISM OF ZnO/GRAPHENE/NICKEL FOAM VIA EXPERIMENTAL AND DFT STUDY

To quantitatively determine the charge transfer mechanism and the energy band alignment of the ZnO/graphene/Ni-foam, the band edge positions were determined using the Mulliken electronegativity theory. As detailed in Section 3.10.1, the CB and VB for ZnO were based on its absolute electronegativity ($X = 5.76$ eV) and the optical band gap ($E_g = 3.08$ eV) obtained from UV-Vis analysis. The resulting CB and VB values for ZnO were calculated to be -0.28 eV and 2.80 eV, respectively. The detailed calculations are provided in Appendix A.

The calculated energy levels illustrate a charge transfer pathway for the ZnO/graphene/Ni-foam photoanode under illumination (Figure 4.38). The calculated energy levels shows that the favourable pathway for photogenerated $e^- - h^+$ pairs under light illumination is from ZnO to graphene, then to Ni. The mechanism can be explained by four steps: (i) the photogenerated electron in the CB of ZnO excite and move toward the graphene layer, (ii) the graphene as a highly conductive bridge facilitates the rapid transport of these electron toward the Ni-foam substrate, (iii) the electron are transfer to the Pt counter electrode through an external circuit and reduce H^+ ions to produce H_2 , and (iv) simultaneously, the photogenerated hole remain in the VB or migrate to the surface of ZnO and react with O^{2-} ions to generate O_2 . Also, the presence of Na_2SO_3 electrolyte as a hole scavenger effectively extracts these holes at the ZnO/graphene interface, suppressing the recombination of photogenerated $e^- - h^+$ pairs. Furthermore, the porous structure of the Ni-foam enhances electrolyte pathway and provides more

active sites for the PEC reaction. These synergistic factors suppress charge recombination, leading to the enhanced PEC and H_2 production performance.

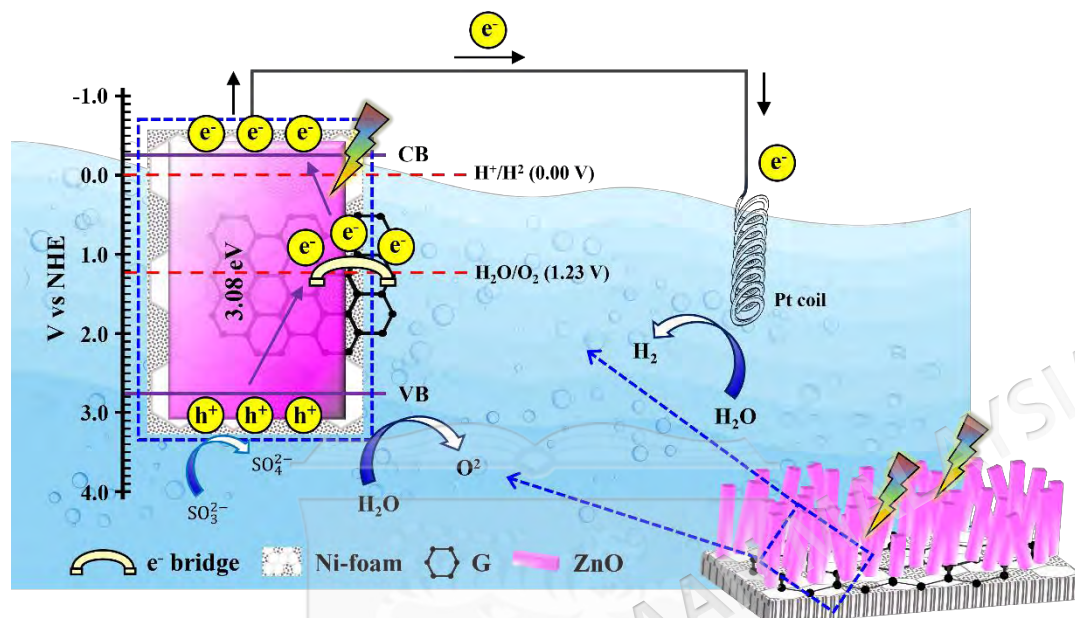


Figure 4.38 Schematic representation of the charge transfer mechanism in the ZnO/graphene/Ni-foam photoanode in 0.50 M Na_2SO_3 electrolyte based on experimental observations.

To validate this mechanism, charge density different (CDD) analysis was performed using DFT calculations. The CDD analysis reveals a clear redistribution of electronic charge that occurs when the ZnO, the graphene layer, and the Ni are integrated. The red regions represent charge accumulation, and blue regions represent charge depletion. The CDD was calculated using Equation (3.18) and illustrated in Figure 4.39 (a). From the ZnO/graphene, a blue region is observed on the surface of zinc atoms, while a red region is concentrated on the graphene layer. This result shows that the electrons are being transferred from the ZnO to the graphene. While for graphene/Ni interface, a significant red region is visible between the graphene layer and the first layer of Ni atoms. This indicates a strong covalent-metallic interaction between graphene and Ni (Hamada & Otani 2010), confirming that electron are further extracted from the graphene into the Ni substrate.

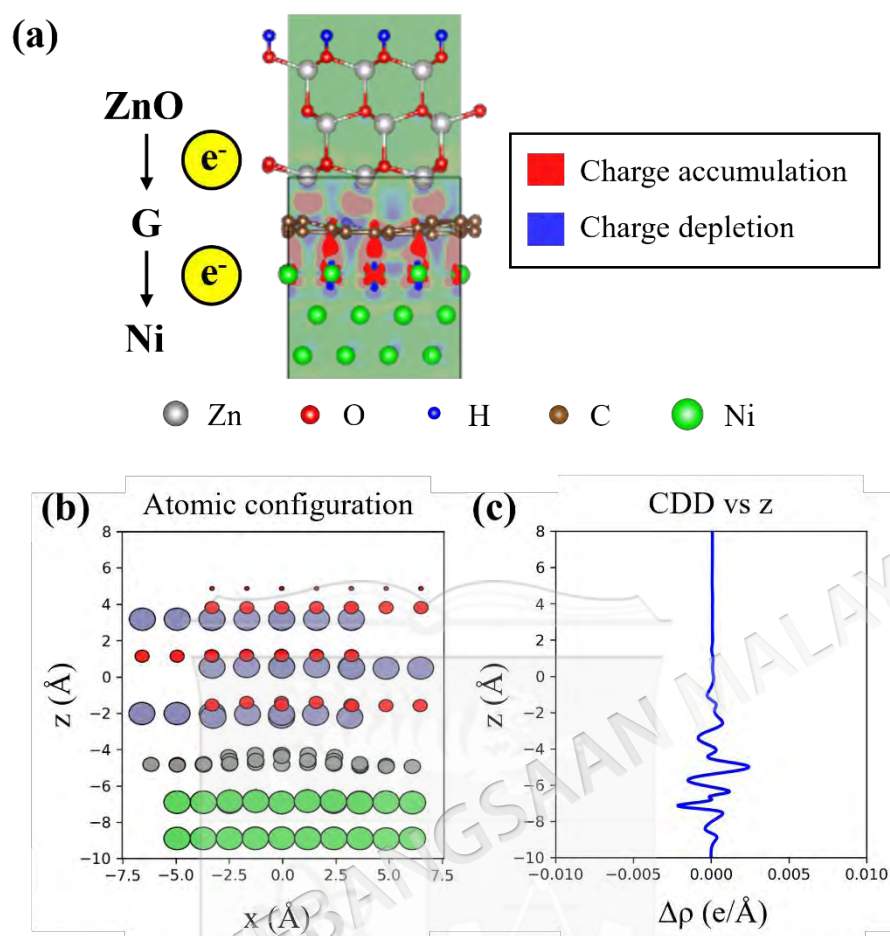
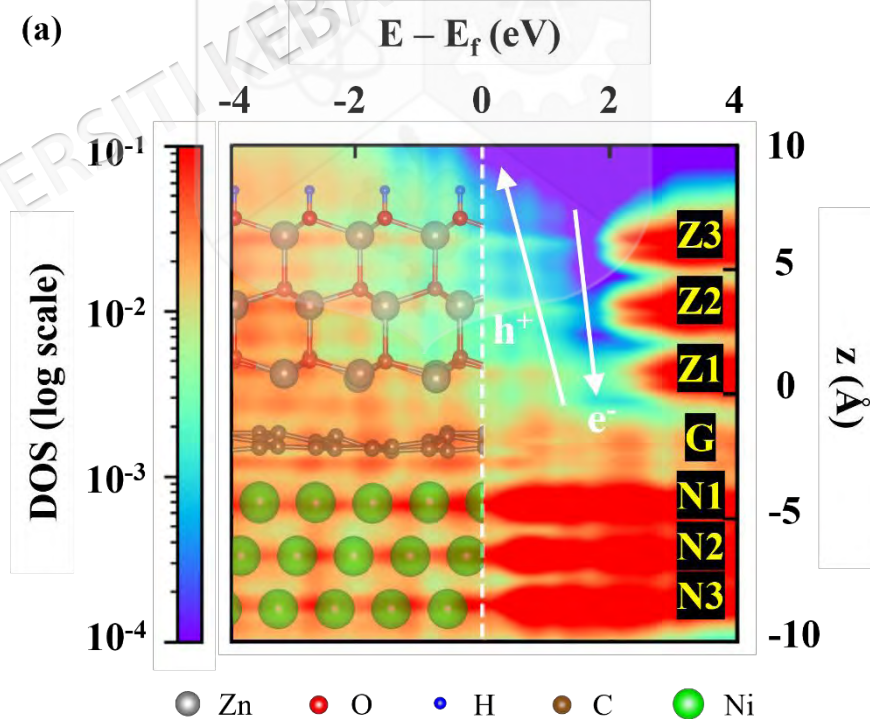


Figure 4.39 Theoretical validation of interfacial redistribution through DFT analysis: (a) CDD isosurface mapping, (b) Atomic configuration of the ZnO/graphene/Ni and (c) The average CDD at z-direction.

The spatial continuity of the charge accumulation where the graphene is sandwiched between the depletion area on the ZnO side and the accumulation on the Ni side provides a proof of the high conductivity bridge mechanism, as seen from the experimental result. Besides, it further supported by the z-direction charge profile (Figure 4.39 (b, c)), which shows a decrease in charge density at the ZnO (0 Å), increase to the graphene layer, then transfer to Ni. The accumulation of electron on the graphene occurs within the π -orbital of carbon atoms (Xu et al. 2013). This demonstrates that the graphene layer facilitates the rapid bridge electron transport and providing a low-resistance pathway for photogenerated electron.

Finally, the combination of experimental results and DFT study allow for the construction of a complete charge transfer mechanism (Figure 4.40). While n-type semiconductors typically exhibit upward band bending (as mentioned in Chapter II (Figure 2.4)), the Layer Density of State (LDOS) analysis reveals a downward band bending at the ZnO interface. This observation suggests the formation of an accumulation layer at the interface of ZnO–graphene and graphene–Ni, establishing an Ohmic contact that significantly reduces the R_{ct} , as confirmed with the EIS result (Figure 4.26). In addition, this downward band bending and interfacial energy level are experimentally validated by the Mott-Schottky analysis (Figure 4.27). The positive slopes observed for all samples confirms the preservation of n-type semiconductor behaviour. Furthermore, the presence of Na_2SO_3 as hole scavenger effectively mitigates the recombination losses usually associated with the downward band bending. The rapid kinetics of the hole scavenger ensure efficient surface oxidation, thereby enhancing charge separation while preserving the inherent n-type bulk properties of the ZnO (Guo et al. 2018; Mahmud et al. 2026).



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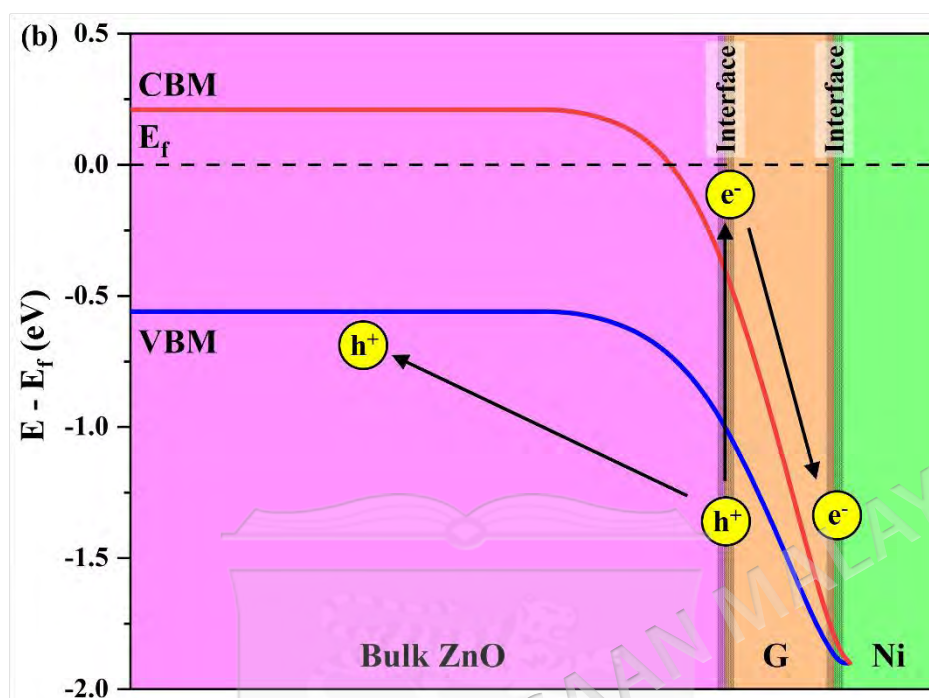


Figure 4.40 Charge transfer mechanism of the ZnO/graphene/Ni-foam based on experimental and DFT results: (a) LDOS showing the electronic coupling at the interface and (b) Band bending diagram illustrating the pathway for photogenerated electron-hole pairs.

When evaluated under PEC operating conditions, the interfacial configuration plays an important role in governing the performance of the photoanode. Under simulated solar illumination, the Ohmic contact formed at the interface facilitates the rapid extraction and transport of photogenerated electrons while suppressing $e^- - h^+$ recombination within the ZnO/graphene/Ni-foam, thereby contributing to an enhanced photocurrent density. This behaviour is driven by the alignment of the E_f within the trilayer configuration, which establishes a built-in electric field across the interface. As a result, photogenerated electrons are efficiently transferred from the CB of the ZnO, through the graphene bridge, and directly to the Ni-foam. This interfacial charge transfer mechanism explains the high efficiency PEC performance of the ZnO/graphene/Ni-foam as photoanodes for H_2 production.

4.9 CONCLUSION

Overall, this chapter established the structure and performance relationships of the ZnO/graphene/Ni-foam through combined experimental and theoretical studies. The results demonstrate that the synergistic effects between ZnO, graphene, and Ni-foam significantly enhance the PEC performance and H₂ production efficiency. Furthermore, the structural and electronic quality of the photoanode was found to be highly dependent on precise synthesis control. For CVD synthesis of graphene/Ni-foam, the quality of the graphene layer was determined by the annealing time (50 minutes), CH₄ flow rate (10 sccm), and the growth time (20 minutes). The optimization of these parameters ensured uniform coverage and the ideal thickness required to facilitate rapid $e^- - h^+$ transport. For hydrothermal growth of ZnO on graphene/Ni-foam, the reaction temperature significantly influenced the morphology of the ZnO nanostructures. By optimizing this temperature together with the utilization of graphene/Ni-foam, highly crystalline 1D nanorods were obtained. It does not only narrow the E_g , improving the light absorption but also strengthen the interfacial chemical bonding between the ZnO and the graphene/Ni-foam, hence lower the onset potential, increased the photocurrent density with small R_{ct} and resulting in higher H₂ production rate as well as the STH efficiency.

The superior performance was validated through an experimental and theoretical approach. DFT calculations confirmed that the ternary configuration (ZnO/graphene/Ni) significantly improve the stability of the photoanode. Both studies consistently indicate the direction charge transfer pathway: ZnO $\Rightarrow$ graphene $\Rightarrow$ Ni. This high efficiency of the ZnO/graphene/Ni-foam photoanode for solar H₂ production is attributed to four main factors: (i) the 3D Ni-foam substrate, where the porous architecture not only provide more active sites for PEC reaction but also facilitates deep electrolyte pathway to ensure maximum surface interaction, (ii) the graphene conductive bridge, helps to reduces the interfacial energy barrier and provides a high-mobility pathway for electron transport from the ZnO to the Ni-foam, (iii) the hole scavenger, where Na₂SO₃ electrolyte effectively captures photogenerated hole at the ZnO surface, suppressing rapid recombination and allowing electron to move freely through the ZnO/graphene/Ni-foam, and lastly, (iv) the 1D ZnO nanorods structure,

which the high aspect ratio of the nanorods provides a direct path for photogenerated $e^- - h^+$ pairs and increases the effective surface area for the PEC reaction.

The results demonstrate that the ZnO/graphene/Ni-foam is a highly promising photoanode for sustainable H_2 production. By bridging the gap between the fundamental materials science and renewable energy application, this research directly contributes to the SDG, specifically with SDG 7 and SDG 13.



CHAPTER V

CONCLUSION AND FUTURE WORK

5.1 CONCLUSION

This study successfully synthesized and developed ZnO/graphene/Ni architecture as a photoanode for photoelectrochemical (PEC) water splitting. It was systematically conducted according to four main objectives, each addressing specific aspects of material synthesis, structural optimization, and performance evaluation. Through the integration of experimental design, advanced characterization techniques, and theoretical analysis, this work provided a comprehensive understanding of charge transfer mechanisms of how the structural and electronic properties of the ZnO/graphene/Ni system influence its PEC performance.

The first objective was to investigate the effect of Chemical Vapor Deposition (CVD) parameters on the morphological and structural properties of graphene grown on a nickel-based conductive metal substrate. Between Ni-foil and Ni-foam, Ni-foam exhibited the most favorable characteristics, including high surface area and porosity, making it a suitable substrate for photoelectrode preparation. Characterization using FESEM, EDX, and Raman analysis confirmed the successful synthesis of graphene on Ni-foam via CVD method, with the best conditions of 50 minutes annealing time, a CH₄ flow rate of 10 sccm, and a growth time of 20 minutes. Under these conditions, a uniform and thin graphene layer with excellent surface coverage on Ni-foam was obtained. These results highlight that the graphene/Ni-foam demonstrates strong potential as a conductive and stable substrate for subsequent ZnO deposition in photoelectrode preparation.

The second objective focused on examining the effect of hydrothermal reaction temperature on the physicochemical properties of ZnO deposited on the graphene/Ni-

foam. The results from FESEM are well-aligned with XRD, where both the dimensional and crystallinity of ZnO structures increased with increasing hydrothermal reaction temperature. Among the examined conditions, the sample synthesized at 200 °C produced well-defined hexagonal rod-like structure of ZnO with an average diameter and length of 2.28 μm and 22.11 μm , respectively. This morphology was attributed to enhanced crystal growth at higher temperatures, which promote the formation of more ordered and uniform distributed ZnO nanorods. Moreover, UV-Vis analysis revealed an E_g of 3.08 eV for the ZnO/graphene/Ni-foam. Consequently, the ZnO/graphene/Ni-foam synthesized at 200 °C exhibited the highest photocurrent density among all samples, indicating more efficient charge separation and transfer. The improvement was primarily attributed to the high crystallinity of ZnO and the role of graphene as a highly conductive electron transport pathway, which effectively reduces charge recombination losses. These combined effects further enhance the interfacial charge transfer kinetics and significantly improve the overall PEC performance.

The third objective evaluated the PEC activity of the ZnO/graphene/Ni-foam photoelectrode in a 0.5 M Na_2SO_3 electrolyte solution. ZnO/graphene/Ni-foam displayed n-type semiconductor behavior as confirmed by Mott-Schottky analysis, promoting efficient charge separation and electron transport. Compared to the control sample (Ni-foam), the ZnO/graphene/Ni-foam demonstrated a significantly higher photocurrent density of 29.04 mA/cm^2 vs RHE, improved stability, and superior performance with 1.72 mL/hour of H_2 production rate (increased by 16.86%). This yielded a STH efficiency of 2.81%. These enhancements were attributed to the synergistic effects from the ZnO/graphene/Ni-foam, where the formation of 1D hexagonal rod-like ZnO structures with high surface area, which provided more active sites for PEC reactions. Moreover, the use of Na_2SO_3 as an electrolyte effectively suppressed $\text{e}^- - \text{h}^+$ recombination through its hole-scavenging ability. It is important to note that graphene acts as a high-conductive electron bridge, facilitating rapid charge transfer and successfully reducing the onset potential. Not to forget, the porous structure of the Ni-foam helps to increase electrolyte pathway as well as provide more sites for PEC reaction. Overall, these findings establish the ZnO/graphene/Ni-foam as a promising photoelectrode material for efficient and stable PEC H_2 generation.

Finally, to achieve objective 4, the charge transfer mechanism between ZnO and graphene/Ni substrate as photoelectrode was elucidated through both experimental characterization and DFT study. Experimental findings revealed that electron are transferred from the CB of ZnO to the graphene, which acts as a conductive bridge for electron before being transfer to the Ni-foam substrate. These results are validated by the DFT study, where the Zn-terminated ZnO/Top-fcc graphene/Ni configuration exhibited downward band bending, facilitating the directed flow of $e^- - h^+$ movement. Furthermore, DFT calculations demonstrated that the combination of ZnO/graphene/Ni is more stable compared to ZnO/graphene or graphene/Ni interfaces, as evidenced by its more negative binding energy. The calculated binding energies were -9.26 eV for ZnO/graphene/Ni, compared with -2.90 eV for ZnO/graphene and -4.11 eV for graphene/Ni. This aligns well with experimental observations, as the ZnO/graphene/Ni-foam maintained its structural integrity even after PEC reactions. In summary, these experimental and computational results confirmed that the Zn-terminated ZnO surface provided a more favourable and efficient charge transfer pathway, thereby enhancing the overall PEC efficiency of the ZnO/graphene/Ni-foam photoelectrode.

5.2 FUTURE WORK

This novel ZnO/graphene/Ni-foam photoelectrode demonstrated remarkable PEC result. However, the development of efficient photoelectrodes for PEC is still in its early stages. Several challenges remain to be addressed; therefore, future research should focus on the following directions:

- i. Investigate the effect of electrolyte concentration during PEC measurement (from 0.1 M to 1.0 M). Since 0.5 M is the most used, exploring a wide range of electrolyte concentrations may provide deeper insights into how ion concentration influences charge transfer efficiency and PEC performance.
- ii. Evaluate the PEC performance and chemical stability of the optimized photoanode in non-sacrificial electrolytes across a wide pH range (such as Na_2SO_4 , NaOH, KOH, and H_2SO_4 electrolytes).
- iii. Strategic modification of the ZnO/graphene/Ni-foam is essential, either by incorporating suitable dopants or co-catalysts (such as noble metals, transition

metal oxides, or sulfides), or substituting ZnO with alternative materials grown (such as TiO_2 , WO_3 , Cu_2O , or BiVO_4) on the graphene/Ni-foam. These approaches aim to enhance charge separation efficiency, broaden light absorption into the visible spectrum, and suppress $e^- - h^+$ recombination, thereby improving overall PEC activity and durability.

- iv. Since the DFT results indicate that the charge transfer mechanism depends on the surface termination of ZnO, further characterization using Scanning Tunneling Microscope (STM), X-ray Absorption Near Edge Structure (XANES) or Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) should be conducted to experimentally verify the surface termination.
- v. Tested PEC operation under outdoor conditions is essential to evaluate structural integrity and performance degradation over time. These assessments will provide valuable insights into the material's practical viability and long-term operational reliability for potential industrial applications.
- vi. Measure the Incident Photon-to-Current Efficiency (IPCE) of the optimized ZnO/graphene/Ni-foam photoanode to evaluate its percentage of converted incident photons across the solar spectrum and identify the specific photon energy range contributing to the enhanced the PEC performance.
- vii. Utilize DFT calculations to investigate the effects of defects and surface adsorbates on the electronic properties, charge transfer behavior, and PEC H_2 performance of the ZnO/graphene/Ni-foam photoanode.

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APPENDIX A

CALCULATIONS FOR THE ESTIMATION OF BAND POSITIONS

Based on the absolute electronegativities (X) values, the band positions of the CB and VB for semiconductors can be calculated using Equation (3.14), (3.15), (3.16) and (3.17):

$$X_M = \frac{1}{2}(IP_M + EA_M)$$

$$X_{MX} = (X_M^a X_X^b)^{\frac{1}{(a+b)}}$$

ZnO:

$$X_{Zn} = \frac{1}{2}(9.39 + (-0.6)) = 4.40$$

$$X_O = \frac{1}{2}(13.62 + (1.46)) = 7.54$$

$$X_{ZnO} = (4.40 + 7.54)^{\frac{1}{2}} = 5.76$$

For CB and VB,

$$CB = X + E_0 - \frac{E_g}{2}$$

$$CB = VB - E_g$$

ZnO:

$$CB = 5.76 + (-4.5) - \frac{3.08}{2} = -0.28$$

$$VB = (-0.28) - (3.08) = 2.8$$

APPENDIX B

HYDROGEN PRODUCTION CALCULATION

Faraday Efficiency (FE) of ZnO/graphene/Ni-foam (H₂ production rate: 1.72 mL/hour) was calculated using Equation (3.6) and (3.7):

$$FE (\%) = \frac{\eta_{\text{experiment}}}{\eta_{\text{theoretical}}} \times 100\%, \text{ where } \eta_{\text{theoretical}} = \frac{Q}{2F}, \text{ where } Q = I \times t$$

$$\eta_{\text{theoretical}} = \frac{24.44 \text{ (C)}}{2(96485 \text{ C/mol})}, \text{ where } Q = (0.00453 \text{ A}) \times (5400 \text{ s})$$

$$\eta_{\text{theoretical}} = 0.000126678 \text{ mol}, \quad Q = 24.44 \text{ C}$$

$$\eta_{\text{theoretical}} = \frac{0.000126678 \text{ mol}}{5400 \text{ s}} = 2.35 \times 10^{-8} \text{ mol/s}$$

$$FE (\%) = \frac{\eta_{\text{experiment}}}{\eta_{\text{theoretical}}} \times 100\%$$

$$\eta_{\text{experiment}} = \frac{1.72 \text{ mL/hour}}{1000} = 0.00172 \text{ L/hour}$$

$$\eta_{\text{experiment}} = \frac{0.00172 \text{ L/hour}}{22.4 \text{ L}} = 7.68 \times 10^{-5} \text{ mol/hour}$$

$$\eta_{\text{experiment}} = \frac{7.68 \times 10^{-5} \text{ mol/hour}}{3600 \text{ s}} = 2.13 \times 10^{-8} \text{ mol/s}$$

$$FE (\%) = \frac{2.13 \times 10^{-8} \text{ mol/s}}{2.35 \times 10^{-8} \text{ mol/s}} \times 100\% = 90.92\%$$

STH efficiency of ZnO/graphene/Ni-foam was calculated using Equation (3.8) and (3.9):

$$STH = \left[\frac{(r_{H_2})(\Delta G)}{(P_{in})(A)} \right] \times 100\%$$

$$PV = nRT, \text{ here } n = r_{H_2}$$

$$r_{H_2} = \frac{PV}{RT} = \frac{(1)(0.00172 \text{ L/hour})}{(0.082 \frac{\text{L}(\text{atm})}{(\text{mol})(\text{K})})(25^\circ\text{C} + 273.15 \text{ K})}$$

$$r_{H_2} = \frac{7.035 \times 10^{-5} \text{ mol/hour}}{3600 \text{ s}}$$

$$r_{H_2} = 1.954 \times 10^{-8} \text{ mol/s}$$

$$STH = \left[\frac{(1.954 \times 10^{-8} \text{ mol/s})(237 \text{ kJ/mol})}{(100 \text{ mW/cm}^2)(1.5 \text{ cm}^2)} \right] \times 100\%$$

$$STH = \left[\frac{(4.631 \times 10^{-6} \text{ kJ/s})(1000 \text{ J/s})(1000 \text{ mJ/s})}{(100 \text{ mW/cm}^2)(1.5 \text{ cm}^2)} \right] \times 100\%$$

$$STH = \left[\frac{4.631 \text{ mW}}{(100 \text{ mW/cm}^2)(1.5 \text{ cm}^2)} \right] \times 100\%$$

$$STH = 3.09\% \text{ (assumed FE} = 100\%)$$

$$STH_{\text{actual}} = STH_{100\%} \times FE_{90\%}$$

$$STH_{\text{actual}} = 3.09\% \times 0.9092 = 2.81\%$$



WSL: Ubuntu (WSL)

Terminal

Sessions

View

File Server

Tools

Games

Settings

Macros

Help

Session

Servers

Tools

Games

Sessions

View

Split

MultiView

Terminal

Package

Settings

Help

Quick connect...

User sessions

WSL: Ubuntu

WSL: Ubuntu

WSL: Ubuntu

WSL: Ubuntu

WSL: Ubuntu

WSL: Ubuntu

10.2 WSL-Ubuntu-20.04

12.353551400319

+1.348000139817

4.1328559401190

1

1

4

6.910872447131

+1.312408004685

5.081354271266

1

1

4

-2.303292240412

+4.008114691113

4.7301349413330

1

1

4

2.291080265201

+4.009102369318

4.7319521373210

1

1

4

6.928564648684

+9.999703408645

5.1883961342500

1

1

4

11.591260748015

+3.939877384210

7.1804933991750

1

1

4

-4.604064723409

+3.32703026854

5.6744454558500

1

1

4

+0.086164903568

-5.417033745703

4.3966299596170

1

1

4

4.591558785151

-5.327167996821

5.0816486305670

1

1

4

2.595971633527

-5.345174343351

2.793684114890

1

1

4

0.615588818012

-7.041134677177

0.1756129054210

1

1

4

6.155504617944

-7.153520696041

-0.1596232026900

1

1

1

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-7.151786233312

-0.1638169714970

1

1

1

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-7.76192616676

-0.089464224570

1

1

1

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-0.0714250924810

1

1

1

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-7.752010336877

-0.159606420650

1

1

1

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3.484810317666

0.2288148629120

1

1

1

0.022397331834

3.484417385130

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1

1

1

-0.104976925174

3.596554809965

-0.1767559441280

1

1

1

-6.150501712020

-3.599516534588

-1.0535514062990

1

1

2

0.019119513131

-3.582135832672

-1.2908624035060

1

1

2

6.168553749096

-3.580026082358

-0.0485997455940

1

1

2

-5.285219826295

1.845755286007

-0.985951152390

1

1

2

-3.055975584630

1.764270038974

-1.3057486603000

1

1

2

3.11102318162

1.773937963089

-1.2881514793340

1

1

2

-12.294169110646

0.095396773021

-0.9963537250000

1

1

2

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0.7076506870240

-0.9083394393500

1

1

2

0.007491879881

7.107796803894

-1.0548640845470

1

1

2

-6.162813808686

-5.559450985901

-3.0038595893000

1

1

1

0.006800803444

-3.580138057254

-0.0557731056100

1

1

1

6.166810109086

-5.559733095453

-5.0012343181060

1

1

1

-5.252434599796

1.819948172143

-4.910578556170

1

1

1

-3.091792740339

1.784502533697

-5.0617054921700

1

1

1

3.111178808478

1.788199317146

-5.0542095874990

1

1

1

-12.30059338893

7.112744042106

-9.235517725470

1

1

1

-6.201813349469

7.10373109665

-4.9112677129470

1

1

1

0.001593052560

7.11772443762

-5.0653989240500

1

1

1

0.00780943785

-7.166721927490

-6.1881883962450

1

1

2

6.160213252766

-7.143258943154

-6.1426361265680

1

1

2

Input file

113.1

549

The screenshot displays the Wireshark interface with the following details:

- Menu Bar:** Terminal, Sessions, View, X server, Tools, Games, Settings, Macros, Help.
- Toolbar:** Search, Servers, Tools, Games, Settings, View, Help, Mailbox, Forwarding, Packages, Settings, Help.
- Status Bar:** Quick connect, 1.9 MB (1.9 MB) - 29.4 KB.
- Packet List:**
 - 0. 1.768000000000 - 7.132354285300 - 9.999184902400 1 0 1
 - 12. 353600000000 - 7.132354285300 - 9.999184902400 1 0 1
 - 3. 088400000000 - 1.783088571300 - 9.999184902400 1 0 1
 - 3. 088400000000 - 1.783088571300 - 9.999184902400 1 0 1
 - 9. 265200000000 - 1.783088571300 - 9.999184902400 1 0 1
 - 6. 176800000000 - 3.566177142700 - 9.999184902400 1 0 1
 - 0. 000000000000 - 3.566177142700 - 9.999184902400 1 0 1
 - 6. 176800000000 - 3.566177142700 - 9.999184902400 1 0 1
 - 9. 265200000000 - 3.566177142700 - 11.204915097600 1 0 2
 - 0. 000000000000 - 3.566177142700 - 11.204915097600 1 0 2
 - 6. 176800000000 - 3.566177142700 - 11.204915097600 1 0 2
 - 9. 265200000000 - 1.783088571300 - 11.204915097600 1 0 2
 - 3. 088400000000 - 1.783088571300 - 11.204915097600 1 0 2
 - 3. 088400000000 - 1.783088571300 - 11.204915097600 1 0 2
 - 12. 353600000000 - 7.132354285300 - 11.204915097600 1 0 3
 - 6. 176800000000 - 7.132354285300 - 11.204915097600 1 0 3
 - 0. 000000000000 - 7.132354285300 - 11.204915097600 1 0 3
 - 6. 176800000000 - 3.566177142700 - 13.200165962200 1 0 3
 - 0. 000000000000 - 3.566177142700 - 13.200165962200 1 0 3
 - 6. 176800000000 - 3.566177142700 - 13.200165962200 1 0 3
 - 9. 265200000000 - 1.783088571300 - 13.200165962200 1 0 3
 - 3. 088400000000 - 1.783088571300 - 13.200165962200 1 0 3
 - 3. 088400000000 - 1.783088571300 - 13.200165962200 1 0 3
 - 12. 353600000000 - 7.132354285300 - 13.200165962200 1 0 3
 - 6. 176800000000 - 7.132354285300 - 13.200165962200 1 0 3
- Packet Details:**
 - Ethernet II, Src: Intel(R) Ethernet Controller (3:9:0), Dst: Intel(R) Ethernet Controller (3:9:0), Length: 1440
 - Internet Protocol Version 4, Src: 192.168.1.1, Dst: 192.168.1.100, Length: 60
 - Hypertext Transfer Protocol, GET / HTTP/1.1, Length: 100
- Packet Bytes:** 1440 bytes captured (1440 bytes on interface) (0.000000000000 - 13.200165962200)

The screenshot shows the VESTA software interface with the 'Input file' dialog box open. The dialog box contains a list of elements and their atomic numbers and weights. The elements listed are Zinc (64), Oxygen (8), Hydrogen (1), Carbon (6), and Nickel (28). The atomic numbers are highlighted in yellow, and the atomic weights are highlighted in red. The dialog box also has a 'Quick connect' button and a 'User sessions' list.

Element	Atomic Number	Atomic Weight
Zinc	64	65.380
Oxygen	8	15.9994
Hydrogen	1	1.00784
Carbon	6	12.0107
Nickel	28	58.6930

```

WSL-Ubuntu-20.04
Terminal Sessions View X server Tools Games Settings Macros Help
Session Servers Tools Games Sessions View Split MultExec Tunneling Packages Settings Help

Quick connect...
User sessions
WSL-Ubuntu
WSL-Ubuntu-20.04

WSL-Ubuntu-20.04
~/bin/csh
PBS -q x21
PBS -l select=2:ncpus=64:mpiprocs=64:ompthreads=1
PBS -j oe
PBS -N ESN_rlx_ft_16_62_M16rZn

source /etc/profile.d/modules.csh
module load intel/2020.2.254 intelMPI/2020.2.254

setenv I_MPI_ADJUST_ALLGATHERV 2
setenv I_MPI_PIN 1

cd $(PBS_O_WORKDIR)
ln -fs /home/thanhpn/STATE/src/STATES.6.11k5_H0.25/STATE STATE
ln -fs /home/morikawa/STATE/gncpp/Zn_pbe1A#new.data fort.37
ln -fs /home/morikawa/STATE/gncpp/O_pbe1A#new.data fort.38
ln -fs /home/morikawa/STATE/gncpp/MLda3.1.5A#new.data fort.39
ln -fs /home/morikawa/STATE/gncpp/MLda3.0.5A#new.data fort.39
ln -fs /home/morikawa/STATE/gncpp/C_pbe1A#new.data fort.40
ln -fs /home/morikawa/STATE/gncpp/N_pbe1A#new.data fort.41

ln -fs /home/hanamoto/STATE/src/kernel.dat kernel.dat
ln -fs /home/hanamoto/STATE/src/vdwphi.dat vdwphi.dat

mpirun ./STATE < nfinp_1 > nfout_1
mpirun ./STATE < nfinp_2 > nfout_2
mpirun ./STATE < nfinp_3 > nfout_3
mpirun ./STATE < nfinp_4 > nfout_4
mpirun ./STATE < nfinp_5 > nfout_5
mpirun ./STATE < nfinp_rlx > nfout_rlx
mpirun ./STATE < nfinp_rlx2 > nfout_rlx2
mpirun ./STATE < nfinp_rlx3 > nfout_rlx3
mpirun ./STATE < nfinp_rlx4 > nfout_rlx4
mpirun ./STATE < nfinp_rlx5 > nfout_rlx5
mpirun ./STATE < nfinp_rlx6 > nfout_rlx6
mpirun --machinefile ./hostfile.g308_10 ./STATE < nfinp_3 > nfout_3

"run_vdw.csh" 36L, 1338C

```

Run file

a) Input and output file name

(#) to disable the file

```

WSL-Ubuntu-20.04
Terminal Sessions View X server Tools Games Settings Macros Help
Session Servers Tools Games Sessions View Split MultExec Tunneling Packages Settings Help

Quick connect...
User sessions
WSL-Ubuntu
WSL-Ubuntu-20.04

WSL-Ubuntu-20.04
~/bin/csh
PBS -q x21
PBS -l select=2:ncpus=64:mpiprocs=64:ompthreads=1
PBS -j oe
PBS -N ESN_rlx_ft_16_62_M16rZn

source /etc/profile.d/modules.csh
module load intel/2020.2.254 intelMPI/2020.2.254

setenv I_MPI_ADJUST_ALLGATHERV 2
setenv I_MPI_PIN 1

cd $(PBS_O_WORKDIR)
ln -fs /home/thanhpn/STATE/src/STATES.6.11k5_H0.25/STATE STATE
ln -fs /home/morikawa/STATE/gncpp/Zn_pbe1A#new.data fort.37
ln -fs /home/morikawa/STATE/gncpp/O_pbe1A#new.data fort.38
ln -fs /home/morikawa/STATE/gncpp/MLda3.1.5A#new.data fort.39
ln -fs /home/morikawa/STATE/gncpp/MLda3.0.5A#new.data fort.39
ln -fs /home/morikawa/STATE/gncpp/C_pbe1A#new.data fort.40
ln -fs /home/morikawa/STATE/gncpp/N_pbe1A#new.data fort.41

ln -fs /home/hanamoto/STATE/src/kernel.dat kernel.dat
ln -fs /home/hanamoto/STATE/src/vdwphi.dat vdwphi.dat

mpirun ./STATE < nfinp_1 > nfout_1
mpirun ./STATE < nfinp_2 > nfout_2
mpirun ./STATE < nfinp_3 > nfout_3
mpirun ./STATE < nfinp_4 > nfout_4
mpirun ./STATE < nfinp_5 > nfout_5
mpirun ./STATE < nfinp_rlx > nfout_rlx
mpirun ./STATE < nfinp_rlx2 > nfout_rlx2
mpirun ./STATE < nfinp_rlx3 > nfout_rlx3
mpirun ./STATE < nfinp_rlx4 > nfout_rlx4
mpirun ./STATE < nfinp_rlx5 > nfout_rlx5
mpirun ./STATE < nfinp_rlx6 > nfout_rlx6
mpirun --machinefile ./hostfile.g308_10 ./STATE < nfinp_3 > nfout_3

"run_vdw.csh" 36L, 1338C

ALDOS
PRINT WEIGHT
FERMI LEVEL 0.18966896
NUMBER_OF_LAYER 401
LAYER
-18.629132422600
-18.529132422600
-18.429132422600
-18.329132422600
-18.229132422600
-18.129132422600
-18.029132422600
-17.929132422600
-17.829132422600
-17.729132422600
-17.629132422600
-17.529132422600

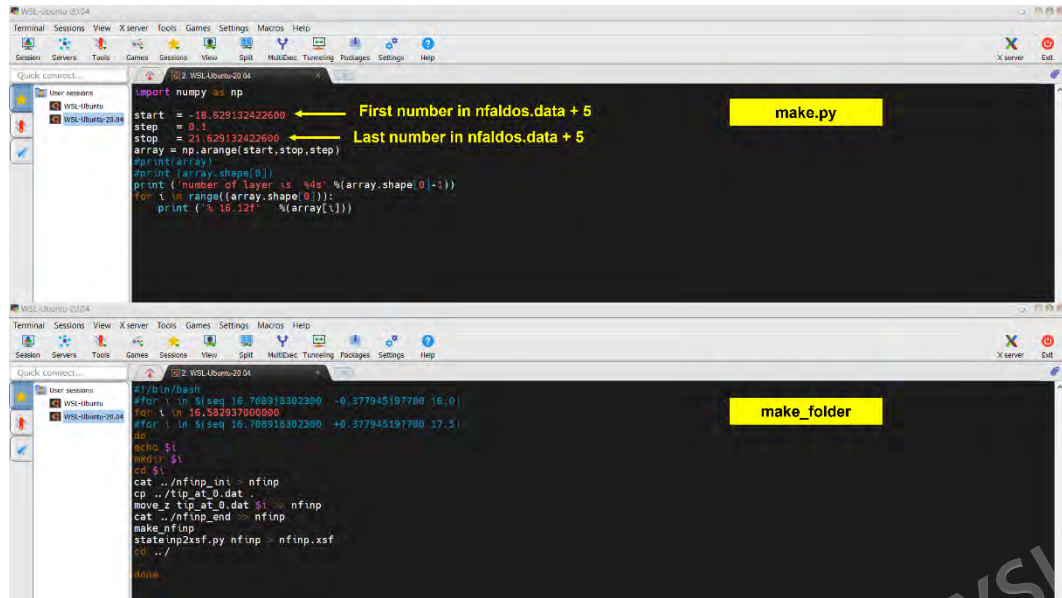
18.470867577401
18.570867577401
18.670867577401
18.770867577401
18.870867577401
18.970867577401
19.070867577401
19.170867577401
19.270867577401
19.370867577401
19.470867577401
19.570867577401
19.670867577401
19.770867577401
19.870867577401
19.970867577401
20.070867577401
20.170867577401
20.270867577401
20.370867577401
20.470867577401
20.570867577401
20.670867577401
20.770867577401
20.870867577401
20.970867577401
21.070867577401
21.170867577401
21.270867577401
21.370867577401
21.470867577401
21.570867577401
ENDIN -15.00
EMAX 5.00
EMIDTH 0.200
WPOOSE 401
WEND

```

Fermi energy "grep -A1 -a FERMI nfout_3"

From aldous.data

nfdalos.data



```

import numpy as np

start = -18.829132422600
step = 0.1
stop = 21.629132422600
array = np.arange(start, stop, step)

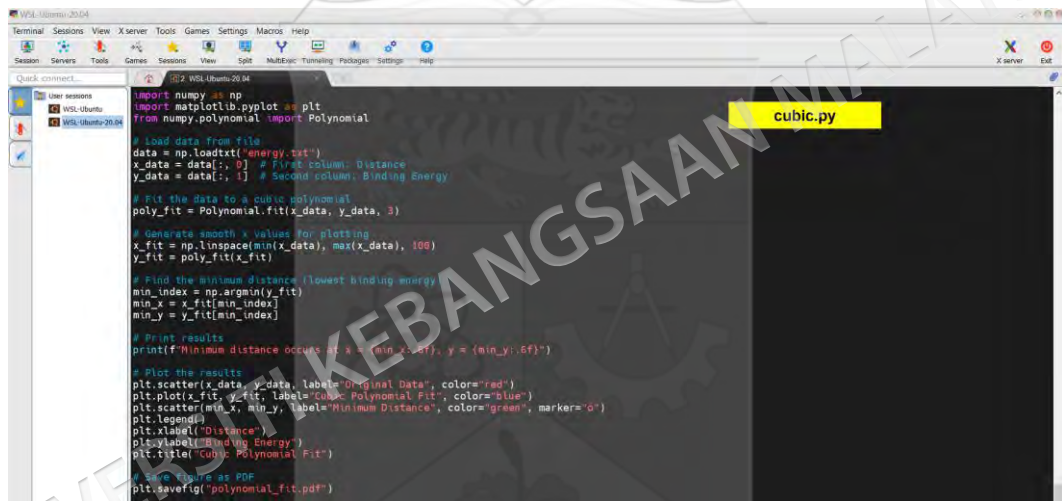
print(array)
print(array.shape[0])
print('number of layer is %4s' % (array.shape[0]-1))
for t in range(array.shape[0]):
    print('%4.12f' % array[t])

```

First number in nfoldos.data + 5

Last number in nfoldos.data + 5

make.py



```

#!/bin/bash
for i in $(seq 16.708918302300 -0.377945197700 16.0)
do
    for t in $(seq 16.582937000000 0.377945197700 17.5)
    do
        mkdir $i
        cd $i
        cp ../nfnip_ini - nfnip
        cp ../tip_at_0.dat - nfnip
        move_z_tip_at_0.dat $i - nfnip
        cat ../nfnip_end - nfnip
        make_nfnip
        stateinp2sf.py nfnip - nfnip.xsf
        cd ../
    done
done

```

make_folder



```

import numpy as np
import matplotlib.pyplot as plt
from numpy.polynomial import Polynomial

# Load data from file
data = np.loadtxt('energy.txt')
x_data = data[:, 0] # First column: Distance
y_data = data[:, 1] # Second column: Binding Energy

# Fit the data to a cubic polynomial
poly_fit = Polynomial.fit(x_data, y_data, 3)

# Generate smooth y values for plotting
x_fit = np.linspace(min(x_data), max(x_data), 100)
y_fit = poly_fit(x_fit)

# Find the Minimum Distance (lowest binding energy)
min_index = np.argmin(y_fit)
min_x = x_fit[min_index]
min_y = y_fit[min_index]

# Print results
print('Minimum distance occurs at x = (min_x:.6f), y = (min_y:.6f)')

# Plot the results
plt.scatter(x_data, y_data, label='Original Data', color='red')
plt.plot(x_fit, y_fit, label='Cubic Polynomial Fit', color='blue')
plt.scatter(min_x, min_y, label='Minimum Distance', color='green', marker='o')
plt.legend()
plt.xlabel('Distance')
plt.ylabel('Binding Energy')
plt.title('Cubic Polynomial Fit')

# Save figure as PDF
plt.savefig('polynomial_fit.pdf')

```

cubic.py

APPENDIX D

LIST OF PUBLICATIONS

Journal publications:

1. **Mohd Shah, N. R. A.**, Mohamad Yunus, R., Rosman, N. N., Wong, W. Y., Arifin, K., Jeffery Minggu, L. 2021. Current progress on 3D graphene-based photocatalysts: From synthesis to photocatalytic hydrogen production. *International Journal of Hydrogen Energy* 46 (14): 9324-9340.
2. **Mohd Shah, N. R. A.**, Mohamad Yunus, R., Rosman, N. N., Wong, W. Y., Arifin, K., Jeffery Minggu, L. 2022. Synthesis of ZnO on 3D Graphene/Nickel Foam for photoelectrochemical water splitting. *Malaysian Journal of Analytical Sciences* 26 (3): 546-553.
3. Rosman, N. N., Mohamad Yunus, R., **Mohd Shah, N. R. A.**, Mohd Shah, R., Arifin, K., Jeffery Minggu, L., Ahmad Ludin, N. 2022 An overview of co-catalysts on metal oxides for photocatalytic water splitting. *International Journal of Energy Research* 46 (9): 11596-11619.
4. Rosman, N. N., Mohamad Yunus, R., **Mohd Shah, N. R. A.**, Arifin, K., Jeffery Minggu, L., Ahmad Ludin, N. 2023. 3D free-standing Graphene: Influence of etching solution and etching time on Chemical Vapor Deposition on the Graphene/Nickel Foam. *Jurnal Kejuruteraan* 35 (1): 231-236.
5. Rosman, N. N., Mohamad Yunus, R., **Mohd Shah, N. R. A.**, Moridon, S. N. F., Arifin, K., Jeffery Minggu, L., Ahmad Ludin, N. 2024. In situ formation of ZnS/Ni₂S₃ with hybrid nanostructure of MoS₂/ZnO on Graphene/Nickel Foam for enhanced photoelectrochemical activity. *International Journal of Hydrogen Energy* 104 (February): 324-335.
6. Rosman, N. N., Mohamad Yunus, R., **Mohd Shah, N. R. A.**, Arifin, K., Jeffery Minggu, L., Ahmad Ludin, N. 2024. Effect of precursor concentrations on ZnO/Graphene/Nickel Foam for photoelectrochemical performance. *Chemical Engineering & Technology* 47: e202300588.

7. Ng, W. S., Azhar, N., **Mohd Shah, N. R. A.**, Rosman, N. N., Saidin, N. U., Muslimin, M., Mohamad Yunus, R. 2024. An overview of catalyst development for enhanced green hydrogen production. *Malaysia Journal of Sustainable Environment* 7 (2): 205-223.
8. Azhar, N., Ng, W. S., **Mohd Shah, N. R. A.**, Zainul Abidin, A. F., Arifin, K., Loh, K. S., Wong, W. Y., Mohamad Yunus, R. 2025. Recent progress and a new perspective of borophene-based catalyst for hydrogen energy applications: A review. *Materials Today Chemistry* 46 (June): 102716.
9. Rosman, N. N., Ng, W. S., **Mohd Shah, N. R. A.**, Masdar, M. S., Karim, N. A., Ataollahi, N., Mohamad Yunus, R. 2025. Nanostructured transition metal-based electrocatalysts: A promising pathway in anion exchange membrane water electrolysis. *Materials Today Sustainability* 31 (July): 101203.
10. **Mohd Shah, N. R. A.**, Rosman, N. N., Mohamed, M. A., Arifin, K., Jeffery Minggu, L., Wong, W. Y., Mohamad Yunus, R. 2026. Controlling the hydrothermal reaction and unlocking the potential of porous substrates for enhanced photoelectrochemical activity in ZnO on Graphene/Nickel Foam. *Sains Malaysiana* 55 (2) (2026): 293-304.

Proceeding:

1. **Mohd Shah, N. R. A.**, Rosman, N. N., Wong, W. Y., Arifin, K., Jeffery Minggu, L., Mohamad Yunus, R. 2022. Effect of annealing time on chemical vapor deposition growth of 3D Graphene for photoelectrochemical water splitting. *Materials Today: Proceedings* 57, 1215-1219.

Book Chapter:

1. Mohamad Yunus, R., Rosman, N. N., **Mohd Shah, N. R. A.** 2023. 3D Graphene as a photocatalyst for water splitting. *3D Graphene: Fundamentals, Synthesis, and Emerging Applications*, 359-374.

APPENDIX E

LIST OF PRESENTATIONS AND AWARDS

Presentations:

1. **Mohd Shah, N. R. A.** and Mohamad Yunus, R. 2021. Effect of annealing time on chemical vapor deposition growth of 3D Graphene for photoelectrochemical water splitting. *International Symposium of Reaction Engineering, Catalysis & Sustainable Energy (RECaSE2021)*.
2. **Mohd Shah, N. R. A.** and Mohamad Yunus, R. 2021. Synthesis of 3D Graphene/ZnO on Nickel Foam for photoelectrochemical water splitting. *Symposium on Fuel Cell and Hydrogen Technology (SFCHT2021)*.
3. **Mohd Shah, N. R. A.** and Mohamad Yunus, R. 2024. Temperature-tuned hydrothermal synthesis on porous substrate: Boosting PEC efficiency of ZnO/Graphene/Nickel Foam. *1st International Symposium on Solar Hydrogen (SSH2024)*.
4. **Mohd Shah, N. R. A.** and Mohamad Yunus, R. 2025. DFT insights on ZnO/Graphene/Ni (111) interfaces for improved PEC properties. *9th International Conference on Fuel Cell & Hydrogen Technology (ICFCHT2025) in conjunction with 12th Conference on Emerging Energy & Process Technology (CONCEPT12)*.

Awards:

1. **Mohd Shah, N. R. A.** 2021. *Kem Maya Olympiad Nanoteknologi Malaysia (ONM2021) Peringkat Kebangsaan* – Bronze Medal.
2. **Mohd Shah, N. R. A.** and Mohamad Yunus, R. 2022. Fabrication of ZnO/Graphene/Nickel Foam photoelectrode for photoelectrochemical water splitting. Fundamental Category in *Virtual International Research and Innovation Symposium and Exposition 2022 (RISE2022)* – Gold medal.
3. **Mohd Shah, N. R. A.** 2022. Development of Zinc Oxide-Graphene Foam photoelectrode for photoelectrochemical hydrogen generation. *Pertandingan*

Projek Penyelidikan Inovasi Nanoteknologi (PIN) Peringkat Kebangsaan – 5th Place.

4. **Mohd Shah, N. R. A.** and Mohamad Yunus, R. 2022-2023. *Quantum Engineering Design Course (QEDC) Short-Term Research Program, Graduate School of Engineering, The University of Osaka, Japan.* – Outbound Mobility.
5. **Mohd Shah, N. R. A.** 2026. Micrograph Art Challenge: “From Grey to Great”. *Karnival Perkhidmatan Instrumentasi & Makmal UKM (INSPIRA) - 2nd place.*

