

IMMOBILISATION OF COPPER (I) OXIDE/ZINC OXIDE NANOPARTICLES ON THE GAS DIFFUSION LAYER FOR CO₂ REDUCTION REACTION APPLICATION

Nor Hafizah Yasin^{1a,b*} and Wan Zaireen Nisa Yahya^{2a}

Abstract: The electrochemical reduction of carbon dioxide (CO₂RR) represents a promising strategy for CO₂ mitigation, requiring highly efficient catalysts integrated into electrochemical devices to achieve high conversion rates and energy efficiencies for desired products. Establishing a gas diffusion electrode is crucial for practical applications of CO₂ electrochemical reduction reactions (CO₂RR). This study uses the air-spraying method to immobilise nano-catalysts onto a gas diffusion layer (GDL) with exceptional homogeneity. A composite of copper(I) oxide (Cu₂O) and zinc oxide (ZnO) nanoparticles in a 4:1 ratio was deposited onto the GDL. Surface morphology analysis revealed the successful immobilisation of cubic Cu₂O and hexagonal wurtzite ZnO with a uniform distribution, indicating potential improvements in CO₂RR performance. Contact angle measurements were conducted to assess surface hydrophobicity, comparing pristine GDL with Cu₂O/ZnO-based GDL. Although the contact angle on the surface of the Cu₂O/ZnO-based GDL slightly reduced from 143.69° to 134.82°, it maintained its hydrophobic nature. This reduction is attributed to Nafion, a binder in the catalyst ink mixture. The sustained high contact angle is crucial for the CO₂ reduction reaction process. X-ray diffraction (XRD) diffractograms of Cu₂O/ZnO-based GDL were compared with reference Cu₂O, ZnO, and bare GDL. The presence of all essential peaks confirms the successful immobilisation. The air-spraying technique effectively achieved a favourable distribution of active metals.

Keywords: Cu₂O/ZnO, gas diffusion layer, immobilisation, CO₂ reduction reaction

1. Introduction

Carbon dioxide is categorized among greenhouse gases (GHG) and is a significant contributor primarily to fossil fuel combustion (Lin et al., 2020; Kim et al., 2015). It is a by-product of natural gas field monetisation within the oil and gas industry (Ahmad Zuhdi et al., 2021; Hassan et al., 2018). With the increasing demand for natural gas, there is a growing exploration of high-CO₂ fields to meet this need. However, the monetisation of high CO₂ fields has led to a rise in global carbon dioxide emissions, contributing to global warming. In response, PETRONAS has set a net-zero carbon emissions target by 2050, emphasizing the necessity for cleaner energy sources. Given the surge in environmental regulations addressing CO₂ emissions, gas field monetisation processes must prioritise fields with fewer contaminants. The depletion of such fields poses a challenge, necessitating urgent strategies to manage the extensive inventories of CO₂ by-products from high CO₂ fields (Hassan et al., 2018).

Effective monitoring of CO₂ emissions is achievable through adopting carbon capture, utilisation, and storage (CCUS). While sequestration remains a primary strategy for handling significant

volumes of CO₂, this approach is characterised by its energy-intensive nature and potential costliness (Hassan et al., 2018; Qiao et al., 2014). In pursuit of alternative solutions, methods involving utilising and converting CO₂ are considered. These approaches aim to generate more value by producing higher outputs of valuable chemicals while concurrently minimising costs (Lin et al., 2020; Qiao et al., 2014).

Exploring reliable pathways such as photoelectrochemical, thermochemical, photocatalytic, and electrochemical routes for converting CO₂ into valuable products is crucial for mitigating global carbon emissions (Yuan et al., 2023; Qiao et al., 2014). Among these methods, the electrochemical route, known as the CO₂ reduction reaction (CO₂RR), stands out as a highly favourable technique. It reduces CO₂ emissions by transforming it into valuable products through heterogeneous electrochemical reduction principles (Lee et al., 2020; De Luna et al., 2018; Lee et al., 2015). CO₂ reduction occurs on the catalytic metal surface of the working electrode, involving two-, four-, six-, and eight-electron reductions, either in an H-cell or flow cell configuration (Yuan et al., 2023; Mowbray et al., 2021; Lin et al., 2020; Qiao et al., 2014). This method has been extensively investigated, yielding valuable products such as methane, carbon monoxide, ethanol, ethylene, formic acid, methanol, and propanol (Lin et al., 2020; Jouny et al., 2018; Qiao et al., 2014). With ongoing research, the prospects for extensive implementation of this technology appear promising.

Authors information:

^aDepartment of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia. E-mail: nor_21001482@utp.edu.my¹, zaireen.yahya@utp.edu.my²

^bPETRONAS Research Sdn Bhd, Lot 3288 & 3289 Off Jalan Ayer Itam, Kawasan Institusi Bangi, 43000 Kajang, Selangor, Malaysia. E-mail: norhafizah.yasin@petronas.com¹

*Corresponding Author: nor_21001482@utp.edu.my

Received: February 7, 2024

Accepted: May 7, 2024

Published: July 31, 2024

Ethylene, a highly versatile product generated through the CO₂ reduction reaction (CO₂RR) process, has significant market value and annual consumption. This chemical is a pivotal raw material in producing various items, including tyres, automotive products, textiles, paint, children's toys, and electronics. Despite the current lab-scale status of ethylene production technology, challenges such as limited ethylene selectivity over other by-products like H₂, resulting from the hydrogen evolution reaction (HER), carbon monoxide, CH₄, and other substances, coupled with drawbacks like a current density below 100 mA/cm² and electrolyser design, have hindered substantial progress toward commercialisation (Yuan et al., 2023). According to Lin et al., the electrochemical reduction technology must fulfil specific criteria to be deemed suitable for commercialisation (Lin et al., 2020). Feasibility for commercialisation hinges on process characteristics meeting certain benchmarks, including a current density within the range of 200-400 mA/cm², a 90% faradaic efficiency, a cell potential below 2.3 V, and a minimum of 30% conversion of CO₂ (Lin et al., 2020).

Since 1989, researchers have investigated the optimal working electrode for the CO₂RR. Copper-based electrodes have emerged as distinctive and efficient catalysts for converting CO₂ into hydrocarbons. While their efficiency has endured, there persists a demand for an active and selective catalyst that can generate specific products (Mok et al., 2023; Yuan et al., 2023; Chen et al., 2021; Chu et al., 2021). The quest for an effective catalyst demonstrating high activity and exceptional selectivity continues. Numerous copper-based working electrodes have been explored, including those with surface modifications geared towards ethylene production from CO₂, such as copper nanoparticles (NPs), copper wire, copper foil, copper oxide-based, bimetallic copper-based, copper-polymer, and copper-MOF (Strijevskaya et al., 2023; Yang et al., 2023; Chen et al., 2021; Chu et al., 2021; Tang et al., 2021; Ivan Merino-Garcia et al., 2019; Hoang et al., 2018; I. Merino-Garcia et al., 2018; Dohyung Kim et al., 2017; Reske et al., 2014). Kim et al. highlighted the efficacy of copper oxide nanoparticles for ethylene production, achieving a faradaic efficiency exceeding 65% (J. Kim et al., 2019). The nano-catalysts were deposited on a glassy carbon electrode and evaluated in a conventional H-cell configuration, with the current density limited to less than 50 mA/cm² due to mass transport limitations. To facilitate the assessment of CO₂RR at higher current densities of 200-400 mA/cm², the integration of the catalyst onto gas diffusion electrodes becomes imperative (Zhang et al., 2019).

This study involves the synthesis of nanosized copper(I) oxide and zinc oxide, applied through air-spraying onto a gas diffusion layer to create copper-based electrodes. In accordance with existing literature (Albo & Irabien, 2016), the inclusion of zinc contributes to the stabilisation of copper ions (Cu⁺) and the elimination of impurities capable of deactivating the electrocatalyst. Moreover, zinc has the potential to mitigate hydrogen formation during the hydrogen evolution reaction (HER), thereby enhancing the overall performance of CO₂ conversion (Merino-Garcia et al., 2019; Keerthiga & Chetty, 2017). There is a gap in the catalyst immobilisation technique on the gas diffusion layer for use in CO₂RR. Previous researchers focused more on the catalyst and CO₂RR performance compared to the

catalyst immobilisation, which is a vital procedure in producing an effective working electrode. With detailed steps, this paper aims to assess the effectiveness of immobilising Cu₂O/ZnO-based gas diffusion layers using the air-spraying technique and characterise the resulting working electrode for potential application in the CO₂RR. The primary objective is to enhance the catalytic efficiency of the gas diffusion layer-based working electrode, particularly when employed in a liquid-flowing system. This enhancement aims to increase the selectivity for ethylene production and improve overall energy efficiency within a CO₂ electroreduction system.

2. Experimental

2.1 Synthesis Preparation of Cu₂O Nanoparticles

Cubic copper(I) oxide (Cu₂O) nanoparticles (NP) were synthesized by dissolving 6g of copper(II) nitrate trihydrate in 30 mL of ethylene glycol with vigorous stirring, heated to 120°C for 20 minutes. The copper solution was then poured into a Teflon-lined sealed reactor. The temperature was gradually increased to a crystal growth temperature of 180°C in an oven and maintained for 7 hours to induce cubic morphology, following the procedure outlined by Jung et al. (Jung et al., 2019). The solution was then cooled to ambient temperature, and the resulting precipitate was subjected to centrifugation and washed multiple times with distilled water and isopropyl alcohol until a clear solution was achieved. The obtained powder was dried overnight at 100°C. The Cu₂O nanoparticle powder was securely stored in a clean and dry Duran bottle for subsequent use.

2.2 Synthesis Preparation of ZnO Nanoparticles

Zinc oxide (ZnO) nanoparticles were synthesized using a modified polyol chemistry method tailored to the available laboratory facilities, following the approach outlined by Mahamuni et al. with modification (Mahamuni et al., 2019). To initiate the synthesis, 6 g of zinc acetate dihydrate was dissolved in 100 mL of triethylene glycol with vigorous stirring, and the mixture was heated to 80°C for 0100 hours. Subsequently, the zinc solution was transferred into a Teflon-lined sealed reactor, and the temperature was gradually increased to 220°C using an oven, maintaining this temperature for 0500 hours. The reaction resulted in the formation of a white precipitate, which was then subjected to centrifugation and washed multiple times with distilled water and ethanol until a clear solution was achieved. The obtained powder was dried overnight at 100°C, and the resulting ZnO nanoparticle powder was stored in a clean and dry Duran bottle for subsequent use.

2.3 Immobilisation of Cu₂O/ZnO Nanoparticles on Gas Diffusion Layer (GDL)

Cu₂O NPs and ZnO NPs were combined in a 4:1 ratio to study the effect of ZnO on the CO₂ reduction performance. Sigracet 39BB carbon paper served as the gas diffusion layer, providing support for the immobilisation of Cu₂O/ZnO. The catalytic ink was formulated by dispersing Cu₂O/ZnO NPs in a 5% Nafion solution, which served as a binder, with isopropyl alcohol (IPA) as the ink deposition carrier. This process followed the methodology outlined in previous studies (Guzman et al., 2021; Jung et al., 2019

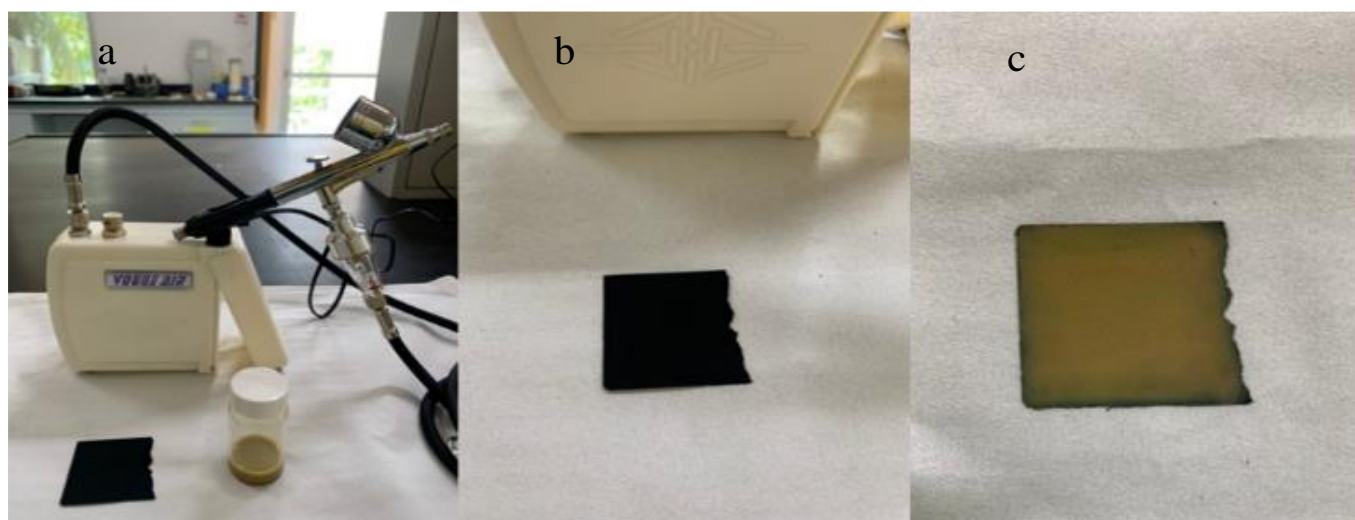


Figure 1. The Setup of a) Air-spraying System for Immobilisation of $\text{Cu}_2\text{O}/\text{ZnO}$ -based GDL, b) neat Gas Diffusion Layer, c) $\text{Cu}_2\text{O}/\text{ZnO}$ -based GDL

I. Merino-Garcia et al., 2018). A mass ratio of 50:50 $\text{Cu}_2\text{O}/\text{ZnO}$ NP with 5 wt% nafion solution was established as the baseline. The solution underwent ultrasonication for 1 hour at ambient temperature to ensure optimal homogeneity. The catalytic layer was then immobilised by spraying the catalyst ink onto the GDL surface and allowing it to dry in an oven for one hour. Figure 1 illustrates the setup of the air-spraying equipment and the colour change of the GDL before and after the immobilisation of $\text{Cu}_2\text{O}/\text{ZnO}$ on its surface.

2.4 Catalyst Characterization

Characterizing $\text{Cu}_2\text{O}/\text{ZnO}$ nanoparticles on the gas diffusion layer (GDL) is essential for evaluating the catalyst's properties. Various characterization methods were employed, as outlined below. A Theta Lite Optical Tensiometer determined the hydrophobicity and hydrophilicity of the gas diffusion electrode (GDE) surface. One centimetre (cm) samples of both the pristine GDL and $\text{Cu}_2\text{O}/\text{ZnO}$ -based GDL were tested. Hydrophobicity was assessed by dropping distilled water on the GDE surface and measuring the contact angle. A Hitachi SU8020 Field Emission Scanning Electron Microscope coupled with Energy Dispersive X-Ray (FESEM-EDX) was utilized to examine the surface morphology of the pristine GDL and $\text{Cu}_2\text{O}/\text{ZnO}$ -based GDL. Both surface and cross-sectional morphologies of the bare GDL and modified GDL were analyzed for structural comparisons at 10K and 40K magnifications. Simultaneously, EDX was employed to identify the elemental compositions and distribution of active metals on the surface and cross-section of the $\text{Cu}_2\text{O}/\text{ZnO}$ -based GDL. For an in-depth analysis of inorganic and nanomaterial phase purity as well as crystallinity properties, X-ray diffraction (XRD) was performed using the Shimadzu XRD-7000 over a range of 30-80 2θ . This technique was applied to both the pristine GDL paper and the $\text{Cu}_2\text{O}/\text{ZnO}$ -based GDL.

3. Results & discussion

3.1 Hydrophobicity of the $\text{Cu}_2\text{O}/\text{ZnO}$ Immobilized on GDL

The contact angle measurement is imperative for assessing surface hydrophobicity and hydrophilicity, providing insight into a liquid's ability to wet a solid surface. A surface is categorized as hydrophobic if its angle exceeds 90° , while an angle below 90° denotes hydrophilicity. Figure 2 displays the contact angles of the pristine GDL and the GDL modified with $\text{Cu}_2\text{O}/\text{ZnO}$. The average contact angle for the pristine GDL is 143.69° , whereas the $\text{Cu}_2\text{O}/\text{ZnO}$ -based GDL exhibits a reduced angle of 134.82° , indicating a decrease of approximately 6%. Despite this reduction, the surface remains classified as hydrophobic.

This reduction in contact angle may be attributed to the presence of Nafion ionomers acting as binders, which enhance catalyst utilization by promoting ionic connectivity. The Nafion ionomer presents a dual advantage by aiding in the binding of metals to the gas diffusion layer and concurrently enhancing ionic conduction (Ramasamy, 2020). However, the inherently hydrophilic nature of Nafion results in an elevated water content within the pores (Kibria et al., 2019). The preservation of high hydrophobicity is crucial for the success of this technology, as it prevents the flooding of the gas diffusion layer. Flooding could adversely impact the mass transfer of CO_2 to the catalyst layer during experimental runs (Guzman et al., 2021; Mowbray et al., 2021; Lin et al., 2020).

Burdyny and Smith (2019) discovered that the elevated hydrophobicity of the electrocatalyst on the gas diffusion layer played a significant role in enhancing CO_2 reduction efficiency and bolstering the stability of the GDL. The hydrophilic and hydrophobic conditions at the working electrode significantly influence the products generated during CO_2 reduction. A hydrophobic environment fosters the hydrocarbon reaction pathway, leading to enhanced C-C hydrocarbon coupling and thus boosting the formation of ethylene (Chang et al., 2022).

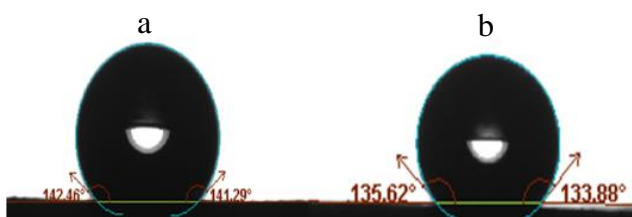


Figure 2. Contact Angle of a) GDL b) immobilized Cu₂O/ZnO-based GDL

3.2 Morphology of the Cu₂O/ZnO Immobilized on GDL

A comparative analysis of FESEM images was conducted at varying magnifications to examine the cross-sectional and surface morphology of both pristine GDL and GDL modified with immobilized Cu₂O/ZnO. Figures 3(a), (b), (e), and (f) depict the cross-sectional views of the pristine GDL and Cu₂O/ZnO-based GDL, respectively. Meanwhile, Figures 3(c), (d), (g), and (h) showcase the surface morphology at magnifications of 10K and 40K.

The results indicate the successful immobilisation of Cu₂O/ZnO nanoparticles on the pristine GDL surface. The catalyst was incorporated into a Nafion solution, serving as a binder, with isopropyl alcohol (IPA) acting as the catalyst carrier during the

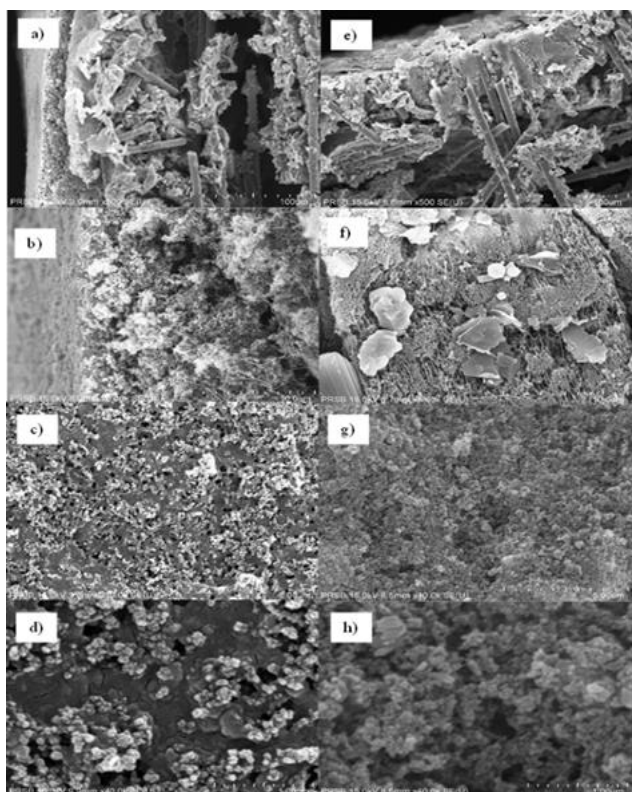


Figure 3. Cross-section and Surface Morphology of a-d) GDL, e-h) Cu₂O/ZnO-based GDL

immobilisation process, following protocols outlined by Guzman et al., Jung et al., and Merino-Garcia et al. (Guzman et al., 2021; Jung et al., 2019; I. Merino-Garcia et al., 2018). The Cu₂O/ZnO

nanoparticles were effectively deposited, providing homogeneous coverage over the GDL surface. Notably, the surface morphologies of the immobilised GDL revealed the cubic shape of Cu₂O and the hexagonal shape of ZnO at both 10K and 40K magnifications.

3.3 Elemental Composition of the Cu₂O/ZnO Immobilized on GDL

Figure 4 depicts the Energy Dispersive X-ray (EDX) spectrum of the gas diffusion layer (GDL), revealing the presence of carbon, fluorine, and oxygen elements. The GDL comprises two primary layers. The first is a microporous layer designed to provide mechanical stability and electrical contact, facilitating gas distribution through macroscale pores composed of carbon structure paper (Kibria et al., 2019). According to Liang et al. (2020), the inclusion of a catalyst in the composition of the GDL prolongs the retention time on the electrode surface, thereby enhancing mass transport and resulting in an augmented current density for CO₂RR.

The second layer, situated between the microporous and catalyst layers, is also microporous and serves to enhance interfacial electrical connectivity while preventing flooding. This is achieved through a combination of carbon black nanoparticles and a hydrophobic polymer mixture. The presence of fluorine is attributed to the inclusion of polytetrafluoroethylene (PTFE) in the GDL compound mixture. PTFE enhances the hydrophobic nature of the GDL, mitigating the risk of flooding during electroreduction reactions.

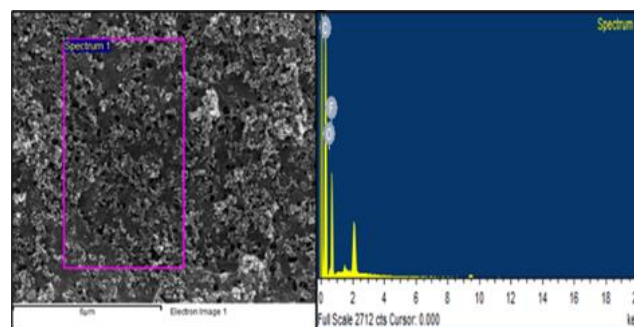


Figure 4. Energy Dispersive X-ray (EDX) Spectrum of GDL

Figure 5 presents the Energy Dispersive X-ray (EDX) spectrum of Cu₂O/ZnO-based GDL. The spectrum reveals the presence of Cu, O, and Zn elements, confirming that the Cu₂O and ZnO compounds were effectively immobilized onto the GDL substrate. The homogeneous distribution of Cu, Zn, and O elements across the gas diffusion layer was achieved using the air-spraying technique. Jong et al. (2013) similarly observed that the air-spraying method results in a more uniform catalyst layer, thereby contributing to improved performance.

Element mapping is employed to assess Cu₂O/ZnO dispersion uniformity on the GDL. In Figure 6, the oxygen atoms are denoted by red dots, copper by blue dots, and zinc by green dots, indicating their distribution on the GDL. The surface crack observed on the catalyst on the GDL is due to the slow evaporation rate of the solvent from the catalyst ink solution during immobilisation. This aspect can be improved by immobilising catalysts on a heated surface, such as a hot plate operating at temperatures ranging from 60 to 80°C.

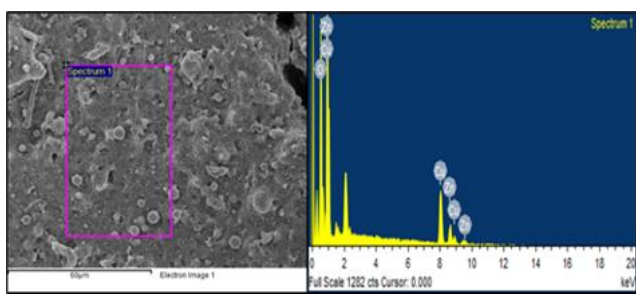


Figure 5. Energy Dispersive X-ray (EDX) Spectrum of Cu₂O/ZnO-based GDL

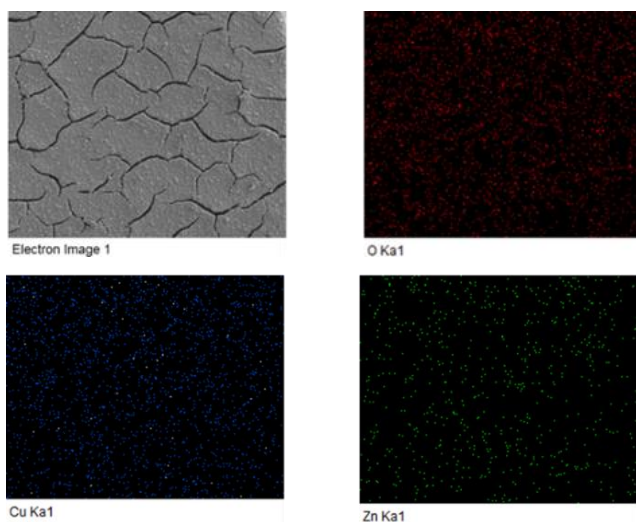


Figure 6: Elements Mapping of Cu₂O/ZnO-based GDL

3.4 Crystalline Structure of Cu₂O/ZnO Immobilized on GDL

Figure 7 illustrates the X-ray diffraction (XRD) patterns of pristine GDL and GDL modified with Cu₂O/ZnO, validating the crystalline structures of the deposited nanoparticles. The XRD diffractogram of Cu₂O/ZnO-based GDL was compared with the pristine GDL, standard Cu₂O (JCPDS 01-078-2078), and ZnO (JCPDS 00-036-1451) patterns to elucidate the crystal structure of these compounds.

The XRD analysis revealed distinct diffraction peaks for the pristine GDL at 37.9°, 44.1°, 54.2°, 64.4°, and 77.5°, as depicted in Figure 7. The immobilized Cu₂O/ZnO-based GDL exhibited all crucial diffraction peaks associated with the Cu₂O cubic crystalline structure (111), (200), and (220) at 36.4°, 42.3°, 52.5°, 61.4°, 65.6°, 69.6°, 73.6°, and 77.4°. This observation aligns with the results reported by Jung et al. (2019), who identified face-centered cubic Cu₂O.

Furthermore, the hexagonal wurtzite crystal structures of ZnO, specifically (100), (002), (101), and (110), were observed on the Cu₂O/ZnO-based GDL surface at 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 66.4°, 67.9°, 69.1°, 72.6°, and 76.9°. The compilation of prominent diffraction peaks corresponding to GDL, Cu₂O, and ZnO in the XRD pattern for Cu₂O/ZnO-based GDL serves as conclusive evidence, affirming the successful immobilisation of the nanocatalyst onto the GDL substrate.

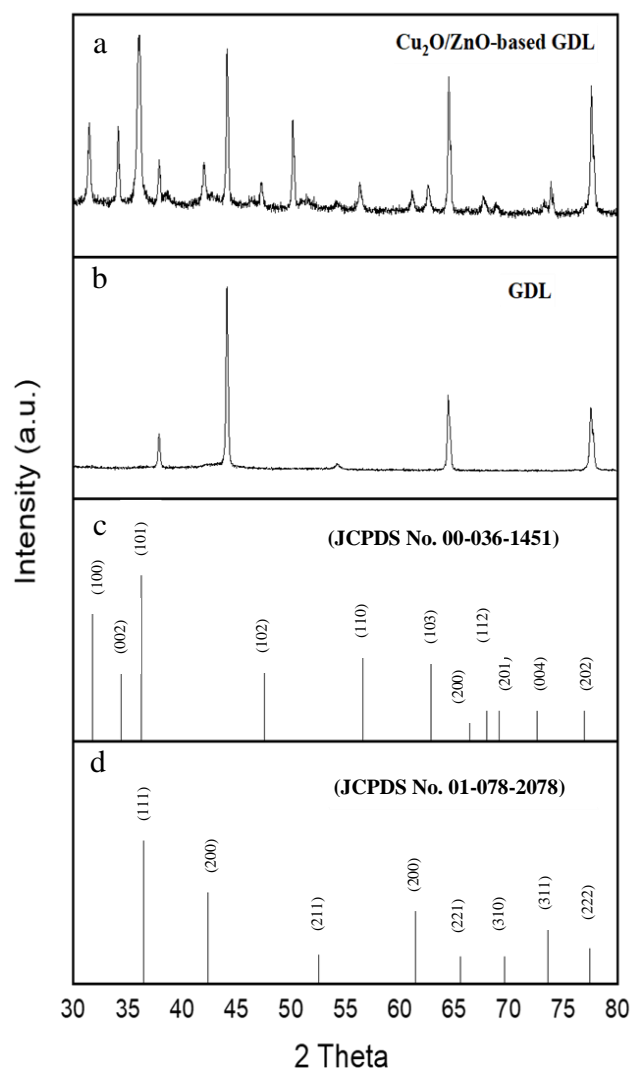


Figure 7. X-ray Diffraction (XRD) Pattern of a) Cu₂O/ZnO-based GDL, b) neat GDL, c) Reference ZnO, d) Reference Cu₂O

4. Conclusion

The deployment of the air-spraying technique for immobilizing Cu₂O/ZnO nanoparticles on the gas diffusion layer (GDL) has been effectively implemented. Detailed examinations of the working electrode's surface morphology, textural properties, and phase characteristics were conducted. The Cu₂O nanoparticles display a cubic structure, while ZnO manifests a hexagonal wurtzite shape, with both uniformly deposited across the gas diffusion layer. The introduction of the Nafion binder resulted in a slight decrease in the hydrophobicity of the Cu₂O/ZnO-based GDL compared to the pristine GDL. Nonetheless, the hydrophobicity level remains acceptable, effectively mitigating the risk of flooding at the working electrode during the liquid flow system's CO₂ reduction reaction process. Projected as an exceptional electrocatalyst for CO₂ reduction reactions, the Cu₂O/ZnO nanoparticle gas diffusion electrode shows considerable potential for future applications.

5. Acknowledgement

The authors acknowledge the support provided by PETRONAS Research Sdn. Bhd. (PRSB) and Universiti Teknologi PETRONAS (UTP).

6. References

- Ahmad Zuhdi, M. F., Rahman, F. H., Shahjavan, H., Mas'od, M. A., Salihuddin, R. S., Zulkepli, N. A., Alias, A., Jalani, M. Y., & Yiin, T. K. (2021). Feasibility Study of Offshore Hybrid Technology for High CO₂ Gas Field Monetization. *Proceedings of International Petroleum Technology Conference*, March, Virtual.
- Albo, J., & Irabien, A. (2016). Cu₂O-loaded gas diffusion electrodes for the continuous electrochemical reduction of CO₂ to methanol. *Journal of Catalysis* 343: 232–239.
- Burdyny, T., & Smith, W. A. (2019). CO₂ reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions. *Energy and Environmental Science* 12(5): 1442–1453.
- Chang, Q., Lee, J. H., Liu, Y., Xie, Z., Hwang, S., Marinkovic, N. S., Park, A. H. A., Kattel, S., & Chen, J. G. (2022). Electrochemical CO₂ Reduction Reaction over Cu Nanoparticles with Tunable Activity and Selectivity Mediated by Functional Groups in Polymeric Binder. *JACS Au* 2(1): 214–222.
- Chen, X., Chen, J., Alghoraibi, N. M., Henckel, D. A., Zhang, R., Nwabara, U. O., Madsen, K. E., Kenis, P. J. A., Zimmerman, S. C., & Gewirth, A. A. (2021). Electrochemical CO₂-to-ethylene conversion on polyamine-incorporated Cu electrodes. *Nature Catalysis* 4(1): 20–27.
- Chu, M., Chen, C., Wu, Y., Yan, X., Jia, S., Feng, R., Wu, H., He, M., & Han, B. (2021). Enhanced CO₂ electroreduction to ethylene via strong metal-support interaction. *Green Energy and Environment* 7(4): 792–798.
- De Luna, P., Quintero-Bermudez, R., Dinh, C. T., Ross, M. B., Bushuyev, O. S., Todorović, P., Regier, T., Kelley, S. O., Yang, P., & Sargent, E. H. (2018). Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction. *Nature Catalysis* 1(2): 103–110.
- Guzman, H., Zammillo, F., Roldan, D., Galletti, C., Russo, N., & Hernandez, S. (2021). Investigation of Gas Diffusion Electrode Systems for the Electrochemical CO₂ Conversion. *Catalysts* 11(4): 482.
- Hassan, H., Omar, N. F. N., Jalil, A. A. M. M., Salihuddin, R. S., & Shah, S. S. M. (2018). Gearing toward CCUS for CO₂ reduction in Malaysia. *Proceedings of Offshore Technology Conference Asia March*, Kuala Lumpur.
- Hoang, T. T. H., Verma, S., Ma, S., Fister, T. T., Timoshenko, J., Frenkel, A. I., Kenis, P. J. A., & Gewirth, A. A. (2018). Nanoporous Copper-Silver Alloys by Additive-Controlled Electrodeposition for the Selective Electroreduction of CO₂ to Ethylene and Ethanol. *Journal of the American Chemical Society* 140(17): 5791–5797.
- Jhong, H. R. Q., Brushett, F. R., & Kenis, P. J. A. (2013). The effects of catalyst layer deposition methodology on electrode performance. *Advanced Energy Materials* 3(5): 589–599.
- Jouny, M., Luc, W., & Jiao, F. (2018). General Techno-Economic Analysis of CO₂ Electrolysis Systems. *Industrial and Engineering Chemistry Research* 57(6): 2165–2177.
- Jung, H., Lee, S. Y., Lee, C. W., Cho, M. K., Won, D. H., Kim, C., Oh, H. S., Min, B. K., & Hwang, Y. J. (2019). Electrochemical Fragmentation of Cu₂O Nanoparticles Enhancing Selective C-C Coupling from CO₂ Reduction Reaction. *Journal of the American Chemical Society* 141(11): 4624–4633.
- Keerthiga, G., & Chetty, R. (2017). Electrochemical Reduction of Carbon Dioxide on Zinc-Modified Copper Electrodes. *Journal of The Electrochemical Society* 164(4): 164–169.
- Kibria, M. G., Edwards, J. P., Gabardo, C. M., Dinh, C. T., Seifitokaldani, A., Sinton, D., & Sargent, E. H. (2019). Electrochemical CO₂ Reduction into Chemical Feedstocks: From Mechanistic Electrocatalysis Models to System Design. *Advanced Materials* 31(31): 1–24.
- Kim, Dahee, Lee, S., Ocon, J. D., Jeong, B., Lee, J. K., & Lee, J. (2015). Insights into an autonomously formed oxygen-evacuated Cu₂O electrode for the selective production of C₂H₄ from CO₂. *Physical Chemistry Chemical Physics* 17(2): 824–830.
- Kim, Dohyung, Kley, C. S., Li, Y., & Yang, P. (2017). Copper nanoparticle ensembles for selective electroreduction of CO₂ to C₂–C₃ products. *Proceedings of the National Academy of Sciences*, 15 August, pp. 10560–10565 United States of America.
- Kim, J., Choi, W., Park, joon woo, Kim, C., Kim, M., & Song, H. (2019). Branched Copper Oxide Nanoparticles Induce Highly Selective Ethylene Production by Electrochemical Carbon Dioxide Reduction 141(17): 6986–6994.
- Lee, M. Y., Park, K. T., Lee, W., Lim, H., Kwon, Y., & Kang, S. (2020). Current achievements and the future direction of electrochemical CO₂ reduction: A short review. *Critical Reviews in Environmental Science and Technology* 50(8): 769–815.
- Lee, S., Kim, D., & Lee, J. (2015). Electrocatalytic production of C₃–C₄ compounds by conversion of CO₂ on a chloride-induced Bi-phasic Cu₂O-Cu catalyst. *Angewandte Chemie - International Edition* 54(49): 14701–14705.
- Liang, S., Altaf, N., Huang, L., Gao, Y., & Wang, Q. (2020). Electrolytic cell design for electrochemical CO₂ reduction. *Journal of CO₂ Utilization* 35: 90–105.
- Lin, R., Guo, J., Li, X., Patel, P., & Seifitokaldani, A. (2020). Electrochemical reactors for CO₂ conversion. *Catalysts* 10(5): .

- Mahamuni, P. P., Patil, P. M., Dhanavade, M. J., Badiger, M. V., Shadija, P. G., Lokhande, A. C., & Bohara, R. A. (2019). Using polyol chemistry for their antimicrobial and antibiofilm activity. *Biochemistry and Biophysics Reports* 17:71–80.
- Merino-Garcia, I., Albo, J., & Irabien, A. (2018). Tailoring gas-phase CO₂ electroreduction selectivity to hydrocarbons at Cu nanoparticles. *Nanotechnology* 29(1):014001.
- Merino-Garcia, Ivan, Albo, J., Solla-Gullón, J., Montiel, V., & Irabien, A. (2019). Cu oxide/ZnO-based surfaces for a selective ethylene production from gas-phase CO₂ electroconversion. *Journal of CO₂ Utilization* 31: 135–142.
- Mok, D. H., Li, H., Zhang, G., Lee, C., Jiang, K., & Back, S. (2023). Data-driven discovery of electrocatalysts for CO₂ reduction using active motifs-based machine learning. *Nature Communications*, 14(7303): 1-12.
- Mowbray, B. A. W., Dvorak, D. J., Taherimakhsousi, N., & Berlinguette, C. P. (2021). How Catalyst Dispersion Solvents Affect CO₂Electrolyzer Gas Diffusion Electrodes. *Energy and Fuels* 35(23): 19178–19184.
- Qiao, J., Liu, Y., Hong, F., & Zhang, J. (2014). A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. In *Chemical Society Reviews* 43(2): 631-675.
- Ramasamy, R.P. (2020). *Membrane Electrode Assemblies*, pp. 787–805, Elsevier B.V.
- Reske, R., Mistry, H., Behafarid, F., Roldan Cuenya, B., & Strasser, P. (2014). Particle size effects in the catalytic electroreduction of CO₂ on Cu nanoparticles. *Journal of the American Chemical Society* 136(19): 6978–6986.
- Strijevskaya, A., Yamaguchi, A., Shoji, S., Ueda, S., Hashimoto, A., Wen, Y., Wardhana, A. C., Lee, J. E., Liu, M., Abe, H., & Miyauchi, M. (2023). Nanophase-Separated Copper-Zirconia Composites for Bifunctional Electrochemical CO₂ Conversion to Formic Acid. *ACS Applied Materials and Interfaces* 15(19): 23299–23305.
- Tang, Z., Nishiwaki, E., Fritz, K. E., Hanrath, T., & Suntivich, J. (2021). Cu(I) Reducibility Controls Ethylene vs Ethanol Selectivity on (100)-Textured Copper during Pulsed CO₂Reduction. *ACS Applied Materials and Interfaces* 13(12): 14050–14055.
- Yang, H., Chuai, H., Meng, Q., Wang, M., Zhang, S., & Ma, X. (2023). Copper-based bimetallic electrocatalysts for CO₂ reduction: From mechanism understandings to product regulations. *Materials Reports: Energy* 3(1): 100174.
- Yuan, L., Zeng, S., Zhang, X., Ji, X., & Zhang, S. (2023). Advances and challenges of electrolyzers for large-scale CO₂ electroreduction. *Materials Reports: Energy* 3(1): 100177.
- Zhang, J., Luo, W., & Zuttel, A. (2019). Self-supported copper-based gas diffusion electrodes for CO₂ electrochemical reduction. *Journal of Materials Chemistry A* 46: 1–9.