# Exploring $BiPO_4$-MWCNT Electrocatalyst for $CO_2$ Reduction to formic Acid (e-fuel)


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## Introduction:

one of the biggest challenges to mitigate the climate change is the increase of carbon dioxide ($CO_2$) in the atmosphere. Transforming $CO_2$ into valuable ,chemicals offers a solution to reduce $CO_2$ concentration in the atmosphere while contributing to sustainable chemical production. Formic Acid (HCOOH) is one of the most promising chemicals that can be produced by electrochemical ,$CO_2$ Reduction Reaction ($eCO_2RR$) due to its applications as a hydrogen carrier and industrial chemical. Formic Acid as a hydrogen carrier offers several favorable properties such as low toxicity, low flammability, and high volumetric hydrogen capacity.

One of the factors that limits the implementation of $eCO_2RR$ to Formic Acid is the lack of highly selective and stable catalyst. Our study will investigate the synthesis and characterization of $BiPO_4$ (BiP) supported on multiwalled carbon nanotubes (MWCNT). Specifically, we investigate the role of MWCNT in enhancing the catalytic properties of BiP , and assess its performance by analyzing its key indicators such as faradic efficiency, selectivity, onset potential, and long-term stability.

By optimizing the properties of the catalyst, this work aims to contribute to the advancement of $CO_2$ utilization technologies and promote the development of greener energy systems.

## Objectives:

-Improving an efficient and highly selective electrocatalyst for electrochemical CO2 reduction reaction to formic acid.

-Evaluate the performance and durability of the catalyst.

-Investigate the electrochemical performance of the BiPO4 /MWCNT as an Electrocatalyst.

-To understand the synergistic effect between BiPO4 and MWCNT in enhancing. catalytic activity and electron transfer.

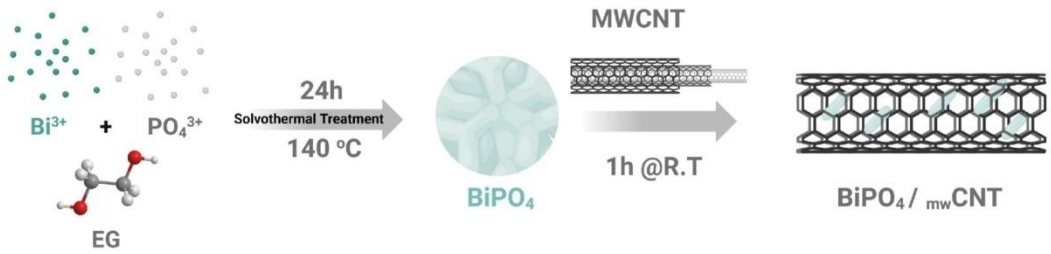
## Methodology and Progress:

The catalysts BiPO4 and BiPO4-MWCNT were tested in an H-cell, were electrochemical characterization and performance tests were applied. H-type cell is a simple setup for preliminary evaluation.

### - catalyst preparation:

-The BiP catalyst was prepared using solvothermal method. $Bi(NO_3)_3$ and $NaPO_4$ salts were used as sources of Bi and $PO_4$, with ethylene glycol as a solvent. The mixture was transferred into the autoclave. After the reaction the catalyst was washed by deionized (DI) water water and ethanol by centrifuge.

-The BiP-MWCNT catalyst was synthesized by mixing the BiP with the MWCNT using ethanol as a solvent. The mixture was sonicated for one hour and then washed by ethanol using centrifuge.




### - Characterization:

-XRD: identify the crystalline structure of the material, and tracks phase changes before and after catalyst.

-XPS: Revels oxidation states, and tracks changes before/after electrolysis to monitor catalyst stability or surface reconstruction.

-SEM: Observes surface morphology, roughness, and porosity of the catalyst Layers.

-Raman: Tracks defect density and functional groups in carbon supports and identifies molecular structures and bonds.

## Electrochemical performance tests:

-Linear sweep voltammetry (LSV)/Cyclic voltammetry (CV): To measure onset potential and reaction kinetics.

-Electrochemical impedance spectroscopy: Provides information on charge transfer resistance.

## Results and findings:

-The incorporation of MWCNT enabled the BiP to be distributed on the surface **Figure 1(b)**, providing more active sites instead of being accumulated in form of nanoclusters **[Figure1 (a)]**.

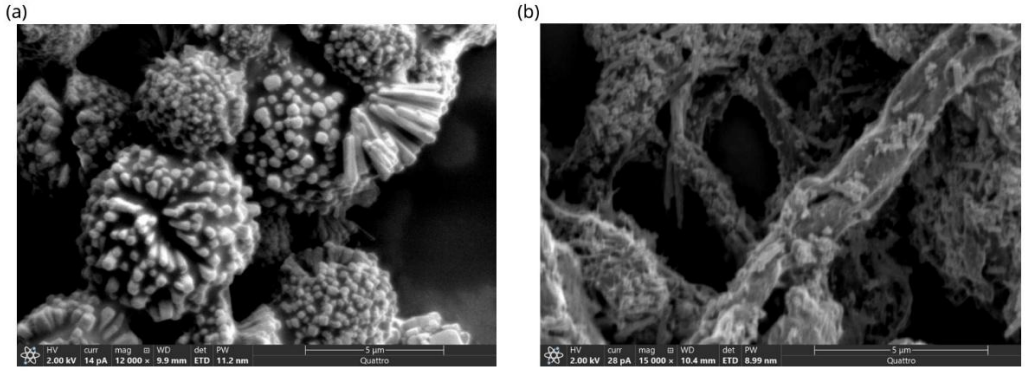



**Figure 1:** (a) SEM of BiP, (b)SEM of BiP-MWCNT

-XRD result demonstrated that the BiP exhibited monoclinic structure, and that MWCNTs interacted well with the BiP **[Figure2(a)]**. The XPS results revealed that the incorporation of MWCNT caused shifting in the peaks and reduced the binding energy of Bismuth and the oxygen **[Figure2(b)].**

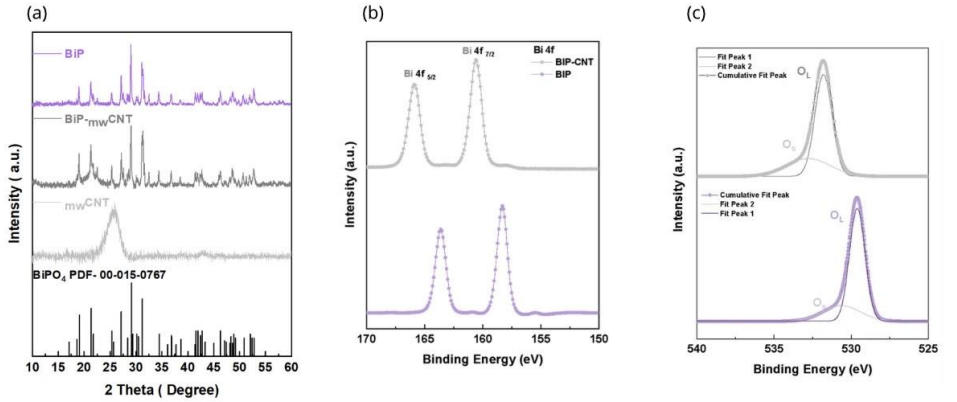



**Figure 2:** (a)XRD results of BiP,MWCNT and BiP-MWCNT, (b)XPS of Bismuth in BiP and BiP-MWCNT ,(c) XPS of Oxygen in BiP and BiP-MWCNT.

- Furthermore, the Raman spectroscopy showed an $I_D/I_G$ ratio of 1for CNT and BiP-MWCNT indicating that no noticeable defects occurred in CNT structure after incorporation BiP **[Figure3]**.

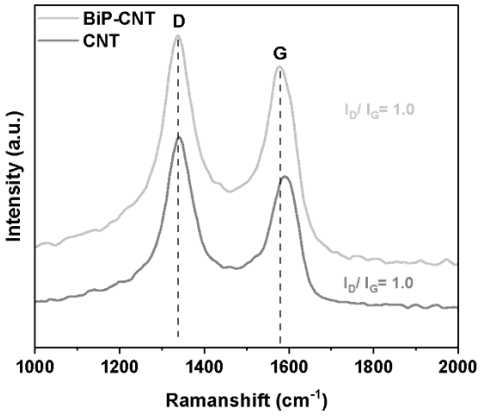



**Figure3:** Raman spectroscopy of CNT and BiP-CNT.

-The incorporation of carbon nanotubes enhanced the charge transfer of the catalyst, which lowered the charge transfer resistance, the onset potential, and increased the current density, which consequently could improve the overall energy efficiency of the reaction **[figure 1]**.

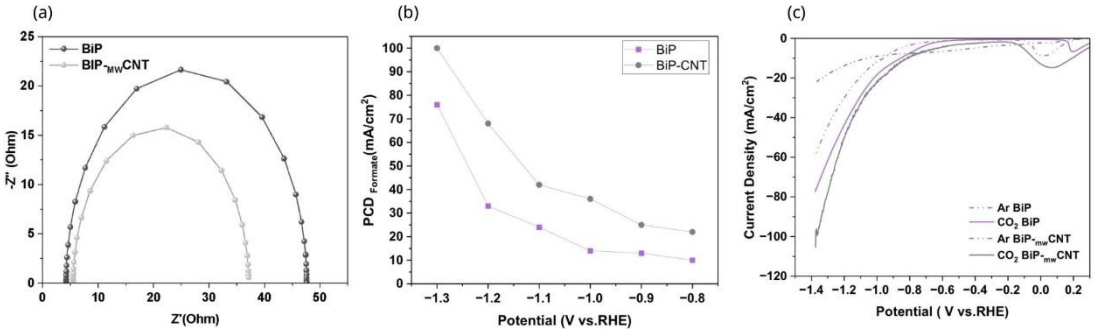



**Figure4:** (a) Electrochemical Impedance spectroscopy of BiP and BiP-CNT. (b) Partial current density of BiP and BiP-CNT. (c) Linear sweep voltammetry.

-Supporting BiP on MWCNT also increased the production rate and enhanced the stability of the catalyst **[Figure5].**

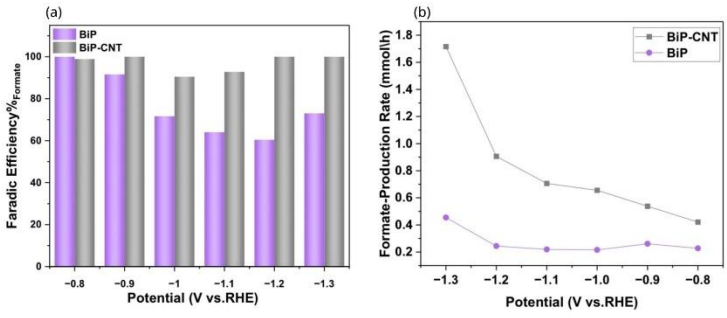



**Figure5:(a)** Faradic efficiency for BiP and BiP-CNT (b) Formate -production rate for BiP and BiP-CNT.

-Stability test: the two catalysts were tested in H-cell. The BiP catalyst exhibited poor stability, lasted only for 16 hours with a low current density. For BiP-MWCNT the catalyst showed improved performance, maintaining stability for about 40 **[Figure6]**.

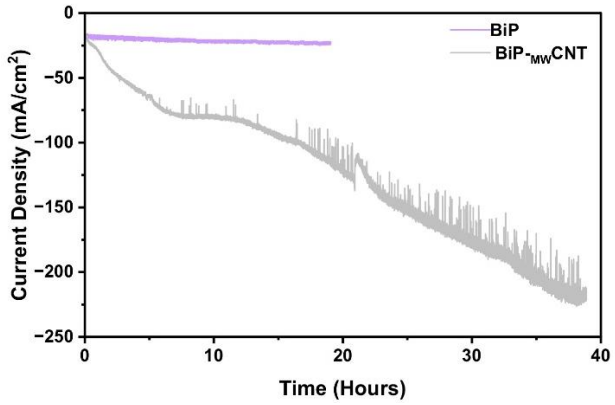



**Figure6:** stability test for BiP and BiP-CNT.

## Challenges:

High current density cannot be achieved in H-cell due to its design limitations.

## Future work:

Testing the BiP-MWCNT catalyst in advance cell design to study its potential for scaling up the formic acid production.

## Conclusion:

In conclusion, development of a stable, efficient, and selective catalyst is essential for the industrial scale production of formic acid. The incorporation of MWCNTs into BiP enhanced the charge transfer, leading to more energy efficient reaction while also improving the stability of the catalyst. These results highlight the rule of MWCNT in improving the catalytic performance. Future work will focus on evaluating the catalyst performance in more advanced cell.

## References:

[1] Adv. Mater. 2024, 36, 2404980

[2] KW-Huang et al., ACS Energy Lett. 2017, 2, 1, 188–195
[3] KW-Huang et al., ACS Energy Lett., 2023, 6, 12, 4390–4394