

A scalable artificial leaf device with high solar-to-fuel efficiency to formate

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Significance and Relevance

This study presents the development of a scalable artificial leaf-type device that integrates a photovoltaic module (PV) with an electrochemical cell (EC) to convert carbon dioxide (CO₂) into valuable chemicals using solar radiation.¹ The research focuses on the successful synthesis and optimization of a CuBi-based gas-diffusion electrode, which demonstrates outstanding performance in reducing CO₂ to formate. A solar-to-fuel (STF) efficiency of 8.3 % is achieved at a current density of 17 mA cm⁻², rising to around 10% also including the co-production of green hydrogen, which is one the highest STF efficiencies reported in the literature. Formate is a promising liquid energy carrier working under ambient conditions, showing potential as a hydrogen carrier in the emerging hydrogen economy. Additionally, this study highlights the role of surface engineering in enhancing electrode properties, such as hydrophilicity and double-layer capacitance, which are crucial to boost performance in CO₂ electrocatalytic reduction powered by solar energy and to scale the artificial leaf prototype for practical applications.²

Preferred topic and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization; CO₂ utilization and recycling Preferred presentation: Oral preferred or Short Oral / Poster

Introduction and Motivations

An artificial leaf is an innovative technology that mimics natural photosynthesis to convert CO₂ into valuable fuels and chemicals using solar energy. This approach offers a sustainable solution for reducing greenhouse gas emissions and generating useful products for industry. The development of efficient and stable electrocatalytic materials/electrodes is crucial for optimizing the performance of photo-electrochemical (PEC) reactors and enabling their scalability. In this work, we developed a highly efficient copper-bismuth (Cu-Bi)-based electrocatalyst with exceptional selectivity to formate production and excellent stability, maintaining strong performance over ten hours of continuous operation. The PEC reactor used for the electrocatalytic tests was designed in a compact configuration to be easily scaled-up and to achieve industrially relevant current densities. The design focused on minimizing ohmic losses and optimizing internal gas and liquid flow pathways and incorporating electrodes with larger catalytic surface area than those typically reported in the literature, thereby enhancing its potential for scale-up operations.

Materials and Methods

The artificial leaf consists of i) a mini-PV module with four silicon heterojunction solar cells and ii) an advanced compact electrochemical cell (EC) made of Plexiglas (Figure 1a). The EC is equipped with a gas chamber for continuous CO_2 supply and operates under illumination from a solar simulator calibrated to provide certified 1 Sun (100 mW cm⁻²). The Cu-Bi electrocatalytic material was synthesized through a simple hydrothermal method, and the final electrodes (with geometrical active area of around 5-10 cm²) were prepared by depositing the resulting Cu-Bi powder onto gas-diffusion layers (GDLs) via spray-coating technique.

Results and Discussion

The artificial cell was validated in two consecutive 5-hour tests to evaluate both performance and stability. Interestingly, during the second 5-hour test, a substantial improvement in the Faradaic



selectivity to formate was observed, reaching a maximum of around 80%. The STF efficiency was calculated as 8.3 %, with the remaining part referred to green H₂ production and minorly to carbon monoxide (CO) formation. This STF value is among the highest reported in the literature, when combined with the achieved current density of 17 mA cm⁻² and cell voltage of 2.5 V. The increasing performance during the second 5-hour test was attributed to the electrochemical activation of the catalyst. To prove this, three further consecutive chronoamperometries were performed at an applied voltage of - 1.2 V, achieving an increase in formate production at the expense of hydrogen (Figure 1b). Advanced *in situ* operando characterization revealed that this improvement was due to the reduction of Cu and Bi species, accompanied by an increase in the hydrophilicity of the catalyst.

Further investigations on the electrode's surface wettability demonstrated that optimizing the physical properties of the electrocatalyst, such as by varying synthesis parameters to enhance hydrophobicity, is critical for addressing selectivity in CO_2 conversion, beyond the nature of the electrocatalytic material itself. Under optimised conditions, a shift in process selectivity from a selective C1 pathway to C2+ products was observed. This can be achieved by modulating hydrogen accessibility through adjustments to the wettability properties of the electrode, opening new routes for designing highly efficient catalysts for CO_2 electrocatalytic reduction.



Figure 1. a) Picture and representative scheme of the artificial leaf for the selective formation of formate by CO₂ reduction b) Faradaic efficiency observed for the CuBi-based electrodes, showing the electrochemical activation of the catalyst during three consecutive chronoamperometries at the same applied potential (-1.2 V vs RHE).

References

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