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Bulk Production of Green Methanol from CO_2 using a Highly Efficient Heterobimetallic Photo-Catalytic System

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Abstract
The conversion of carbon dioxide (CO_2) into value-added fuels and chemicals represents a cornerstone strategy for mitigating climate change while enabling a circular carbon economy. Among various CO_2-derived products, methanol is particularly attractive due to its high energy density, ease of storage and transport, and widespread use as a fuel, hydrogen carrier, and chemical feedstock. This paper presents a comprehensive scientific analysis of the bulk production of green methanol from CO_2 using a highly efficient heterobimetallic photo-catalytic system. Emphasis is placed on catalyst design principles, photo-induced charge transfer mechanisms, reaction pathways, scalability, and sustainability considerations. The synergistic interaction between two distinct metal centers in heterobimetallic photocatalysts enables enhanced light absorption, prolonged charge separation, and improved catalytic activity and selectivity toward methanol formation. The paper integrates fundamental concepts, recent advances, mechanistic insights, and future prospects, highlighting the potential of heterobimetallic photo-catalysis as a scalable and environmentally benign route for green methanol production.

Keywords
Carbon dioxide reduction; Green methanol; Heterobimetallic photocatalyst; Artificial photosynthesis; Sustainable chemistry

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1. Introduction

The unprecedented rise in atmospheric carbon dioxide (CO_2) concentration resulting from extensive fossil fuel combustion has emerged as a major driver of global climate change (1,2). Addressing this challenge requires not only reducing CO_2 emissions but also developing technologies that convert CO_2 into value-added products. Carbon capture and utilization (CCU) has therefore gained significant attention as a complementary strategy to carbon sequestration.

Methanol occupies a central position in CCU strategies due to its versatility as a liquid fuel, hydrogen carrier, and precursor for numerous chemicals such as formaldehyde, acetic acid, and olefins (3,4). The concept of a "methanol economy," wherein renewable methanol serves as a key energy vector, has been widely advocated. Conventional industrial methanol synthesis relies on syngas derived from

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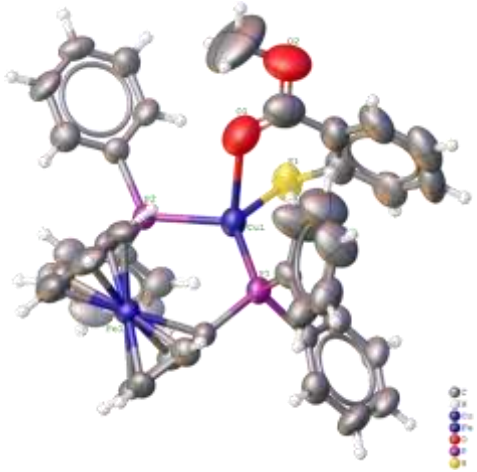
fossil resources, making it energy-intensive and carbon-positive. Consequently, the direct conversion of CO_2 into methanol using renewable energy sources represents a transformative approach toward sustainable fuel production.

Structure of Photocatalyst:



Characterization is done by spectroscopically as well as SC-XRD Technique and already published in NJC 2022 Krishna and *etal*

Photocatalytic CO_2 reduction, inspired by natural photosynthesis, offers a promising pathway to drive thermodynamically uphill reactions under mild conditions using solar energy (5,6). However, achieving high selectivity toward methanol, which requires a six-electron reduction process, remains a major challenge. Recent studies have demonstrated that heterobimetallic photocatalysts can overcome many limitations of monometallic systems by exploiting synergistic interactions between two metal centers. This paper focuses on the principles, performance, and prospects of heterobimetallic photocatalytic systems for bulk green methanol production from CO_2.

2. Fundamentals of Photocatalytic CO_2 Reduction

Photocatalytic CO_2 reduction involves the absorption of light by a semiconductor or molecular photocatalyst, generating excited electrons and holes. The photogenerated electrons participate in reductive processes, while holes are consumed by sacrificial agents or water oxidation reactions. The overall efficiency depends on light absorption, charge separation, charge transport, and surface reaction kinetics.

CO_2 is a thermodynamically stable and kinetically inert molecule, requiring significant activation energy for reduction (Kondratenko et al., 2013). The multi-electron reduction of CO_2 can yield various products, including CO, formic acid, formaldehyde, methanol, and methane. Among these, methanol formation is particularly demanding due to its six-electron, six-proton transfer requirement. Controlling product selectivity therefore necessitates precise catalyst design and reaction engineering.

3. Heterobimetallic Photocatalysts: Design Principles

Heterobimetallic photocatalysts incorporate two distinct metal centers within a single catalytic framework (7). The presence of dual metals enables cooperative effects that are not accessible in monometallic systems. Key design principles include:

1. **Synergistic Electronic Interaction:** One metal center may serve as the primary light absorber, while the second facilitates electron transfer or CO_2 activation.
2. **Efficient Charge Separation:** Spatial separation of reduction and oxidation sites suppresses electron–hole recombination.
3. **Complementary Redox Properties:** Metals with different redox potentials enable stepwise multi-electron transfer processes.
4. **Structural Stability:** Robust metal–metal interactions enhance catalyst durability under prolonged irradiation.

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Earth-abundant metals such as iron, copper, cobalt, and nickel are particularly attractive for sustainable photocatalysis due to their low cost and favorable redox properties (6,7). Iron–copper heterobimetallic systems, for example, combine the strong CO_2-binding ability of iron with the excellent electron-transfer properties of copper, leading to enhanced catalytic performance.

4. Reaction Pathways for CO_2-to-Methanol Conversion

The photocatalytic conversion of CO_2 to methanol proceeds through a sequence of proton-coupled electron transfer steps involving key intermediates such as $CO_2^{\bullet-}$, formate, formaldehyde, and methoxy species (2,4). Heterobimetallic catalysts stabilize these intermediates through metal–ligand and metal–metal cooperative interactions, thereby lowering activation barriers.

A plausible mechanism involves initial CO_2 adsorption and activation at one metal center, followed by stepwise reduction facilitated by electron transfer from the second metal site. This division of labor between metal centers enhances both reaction kinetics and selectivity toward methanol.

5. Bulk Production of Green Methanol

Recent advances have demonstrated that heterobimetallic photocatalytic systems can achieve not only laboratory-scale activity but also bulk methanol production (Chen et al., 2020; Olah et al., 2018). Optimized catalyst formulations, high photon flux, and effective reactor design enable significantly enhanced methanol yields. High selectivity toward methanol minimizes downstream separation costs, improving overall process economics.

Bulk production studies highlight the scalability of heterobimetallic photocatalysis and its potential integration with industrial CO_2 sources. The use of solar or simulated solar irradiation further reinforces the sustainability of the process.

6. Catalyst Characterization and Product Analysis

Comprehensive characterization of heterobimetallic photocatalysts is essential to establish structure–activity relationships. Techniques such as X-ray diffraction (XRD), UV–visible spectroscopy, X-ray photoelectron spectroscopy (XPS), and electron microscopy provide insights into catalyst composition, electronic structure, and morphology.

Methanol formation is typically confirmed using chromatographic techniques such as gas chromatography (GC) or high-performance liquid chromatography (HPLC). Qualitative tests, including characteristic flame tests based on borate ester formation, offer additional confirmation of methanol presence.

7. Sustainability and Environmental Impact

The photocatalytic conversion of CO_2 to methanol aligns closely with the principles of green chemistry and sustainable development (Aresta et al., 2014; Olah et al., 2018). The process utilizes CO_2 as a carbon feedstock, solar energy as a renewable input, and earth-abundant metals as catalysts. When coupled with renewable hydrogen sources or water oxidation reactions, the overall process can achieve near-carbon-neutral or carbon-negative operation.

Life-cycle assessments suggest that green methanol produced via photocatalysis can significantly reduce greenhouse gas emissions compared to conventional fossil-based methanol synthesis.

8. Challenges and Future Prospects

Despite significant progress, several challenges remain before large-scale deployment becomes feasible. These include improving photon utilization efficiency, extending catalyst lifetime, and designing reactors capable of handling industrial-scale CO_2 throughput. Future research should focus on advanced catalyst architectures, tandem catalytic systems, and integration with solar concentrators or photoelectrochemical devices.

The continued development of heterobimetallic photocatalysts holds immense promise for realizing artificial photosynthesis at scale and advancing the global transition toward sustainable energy systems.

9. Conclusion

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Heterobimetallic photocatalytic systems represent a powerful and versatile platform for the conversion of CO_2 into green methanol. By exploiting synergistic metal–metal interactions, these catalysts achieve enhanced light absorption, efficient charge separation, and high selectivity toward methanol formation. The ability to demonstrate bulk methanol production underscores the scalability and practical relevance of this approach. Continued innovation in catalyst design and reactor engineering is expected to further accelerate the adoption of photocatalytic green methanol production as a key component of future carbon-neutral energy infrastructures.

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