Circular carbon and plastic waste valorization via photoelectrochemical H_2 production and CO_2 conversion

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The continuous rise in atmospheric carbon dioxide (CO_2) concentration is one of the most critical drivers of global climate change. Recent measurements indicate that the global average atmospheric CO_2 concentration exceeded 424 ppm in 2024 and is projected to reach approximately 426–430 ppm during 2025, representing the highest level recorded in at least two million years [1]. Compared with the pre-industrial concentration of about 280 ppm, this represents an increase of more than 50%, largely driven by fossil fuel combustion, industrial activities, and land-use change. In parallel with rising CO_2 emissions, plastic waste has become one of the most severe environmental pollution challenges. Global plastic production has exceeded 400 million tons per year, and only a small fraction of this material is effectively recycled. Most plastic waste accumulates in landfills or the natural environment. According to Kim et al. [2], among the different polymer types, polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS) represent the dominant fraction of global plastic waste streams. Polyolefins such as PE and PP alone account for nearly 50% of global plastic waste, making them prime candidates for valorization technologies.

In recent years, carbon capture and utilization (CCU) strategies have been proposed to transform CO_2 from an environmental liability into a valuable feedstock for fuels and chemicals. Among the possible products, methanol and formic acid have attracted particular attention. Methanol is a versatile platform molecule used as fuel, H_2 carrier, and feedstock for the chemical industry, while formic acid can serve as a H_2 storage medium and chemical intermediate [3], [4]. Moreover, photoelectrochemical (PEC) technologies represent a promising approach for the conversion of CO_2 using renewable energy. By combining light absorption, charge separation, and catalytic reactions within integrated systems, PEC processes can convert solar energy directly into chemical fuels. Nevertheless, the efficiency of CO_2 reduction remains limited. Current electrochemical and photoelectrochemical systems typically achieve Faradaic efficiencies ranging from about 20–60% for formic acid, depending on the catalyst and electrolyte conditions, while the production of methanol generally remains lower due to the complexity of the multi-electron transfer reaction [5], [6].

Another major limitation of CO_2 conversion pathways is the availability of sustainable H_2. Conventional production via water electrolysis or steam methane reforming requires significant energy inputs. Recently, PEC plastic waste reforming has emerged as a promising strategy to simultaneously degrade plastic polymers and generate H_2. In these systems, plastic substrates act as electron donors, enabling H_2 evolution while producing valuable oxidation products. Then, integrating plastic waste upcycling with CO_2 conversion technologies offers a promising pathway to simultaneously address plastic pollution, renewable H_2 production, and carbon utilization. This research proposes an integrated approach that couples photoelectrochemical plastic waste upcycling for H_2 production with CO_2 hydrogenation to methanol and formic acid, thereby establishing a synergistic pathway for the valorization of both carbon emissions and solid plastic residues.

The specific objectives of the study include *i) design and development of photoelectrochemical catalytic systems* capable of reducing CO_2 into value-added products such as methanol and formic acid under solar-driven conditions, *ii) investigation of plastic waste upcycling pathways through photoelectrochemical oxidation processes* to produce H_2 while transforming polymers into valuable chemical intermediates, *iii) integration of H_2 generation and CO_2 reduction processes* in order to establish a coupled system for solar-driven fuel and chemical production, *iv) evaluation of energy efficiency and environmental performance*, including sustainability metrics such as energy balance, carbon utilization efficiency, and potential greenhouse gas emission reductions, and *v) assessment of scalability and feasibility*, considering process integration strategies that could contribute to decentralized and renewable fuel production systems.

The proposed research will focus on the development and evaluation of integrated photoelectrochemical systems combining CO_2 reduction and plastic waste upcycling. The methodology will include three main components: catalyst development, system integration, and sustainability assessment. Advanced catalytic materials will be investigated for the selective reduction of CO_2 to methanol and formic acid. Particular attention will be given to nanostructured catalysts and semiconductor photoelectrodes designed to enhance light absorption, charge separation, and catalytic selectivity.

The performance of these systems will be evaluated through key electrochemical parameters including: i) Faradaic efficiency, ii) current density, iii) product selectivity, and iv) solar-to-fuel efficiency. These indicators are commonly used to assess the effectiveness of photoelectrochemical fuel production systems. As for the plastic waste upcycling for H_2 production, the anodic reaction of the photoelectrochemical system will involve the oxidation of plastic waste streams. These polymers represent a large fraction of global plastic waste and are therefore promising feedstocks for plastic upcycling technologies. As depicted by Li et al. [7], through photoelectrochemical oxidation processes, these polymers can be converted into smaller organic molecules while simultaneously generating protons and electrons that drive hydrogen evolution at the cathode. The H_2 fraction generated in this step can subsequently be used to facilitate the hydrogenation of CO_2 into methanol and formic acid.

Regarding the techno-economic and sustainability assessment, a comprehensive sustainability assessment will be conducted using process modeling and techno-economic analysis (TEA). The performance indicators on each dimension to be considered are listed in **Table 1**. These metrics will allow the identification of key technological bottlenecks and will provide insights into the scalability of integrated photoelectrochemical systems for renewable fuel production [8].

Table 1. Indicators evaluated in each dimension.

Technical indicators	Economic indicators	Environmental indicators
1. CO_2 conversion efficiency.	1. Levelized cost of methanol (LCOM).	1. Life-cycle greenhouse gas emissions.
2. H2 production rate.	2. Levelized cost of hydrogen (LCOH).	2. Energy returns on energy invested (EROI).
3. Process mass intensity.	3. Capital expenditure (CAPEX).	
4. Solar-to-fuel efficiency.	4. Operational expenditure (OPEX).	
5. Carbon utilization efficiency.	5. Payback period.	

The proposed research is expected to contribute to the development of innovative technologies for the sustainable production of fuels and chemicals. By combining CO_2 utilization with plastic waste upcycling, the proposed approach aims to establish a synergistic pathway for addressing two major environmental challenges simultaneously. The integration of photoelectrochemical processes could enable the production of solar fuels such as methanol while reducing reliance on fossil resources. Methanol produced from captured CO_2 supports the transition toward a low-carbon energy system. Furthermore, the use of plastic waste as a feedstock for H_2 production represents a promising strategy for waste valorization. Instead of being disposed of or incinerated, plastic materials could be transformed into valuable chemical intermediates while contributing to the generation of renewable fuels. From a broader perspective, this research supports the development of circular carbon technologies, where carbon atoms are continuously recycled rather than emitted into the atmosphere. The integration of solar energy, CO_2 utilization, and waste upcycling aligns with global efforts to promote sustainable energy systems and resource efficiency.

This work proposes an integrated photoelectrochemical strategy for the simultaneous valorization of carbon dioxide and plastic waste. By coupling H_2 production from plastic waste upcycling with CO_2 reduction to methanol and formic acid, the proposed system seeks to develop a sustainable pathway for renewable fuel production. The combination of advanced catalytic materials, solar-driven electrochemical processes, and sustainability assessment will provide insights into the feasibility and potential impact of these technologies. Ultimately, such integrated systems could play a key role in advancing carbon circularity, reducing greenhouse gas emissions, and promoting the sustainable management of solid waste resources.

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