Multilayered $BiVO_4/WO_3$/perovskite-based photoanodes for solar-driven CO_2 photoelectroreduction to formate

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Highlights

- A perovskite-based photoanode has been successfully developed for an improved PEC CO_2 reduction to formate.
- The optimal $CaTiO_3$ loading (1 mg cm^{-2}) could reach up to -71 mA cm^{-2} at -1.8 V (vs. Ag/AgCl) in the cathode.
- $BiVO_4/WO_3$ (80:20) photoanode exhibits the best PEC response under visible light illumination.

1. Introduction

Despite being one of the most promising utilization strategies from both economic and environmental perspectives, the electrochemical reduction of CO_2 presents limitations associated with the energy required to break CO_2 bonds. Integrating photoactive materials in the anode compartment of electrochemical reactors has the potential to reduce overall energy consumption by generating an extra electron flow from light over the anode surface, which can then be transported to the cathode for enhanced CO_2 reduction [1]. In this sense, perovskite materials, such as $CaTiO_3$, have demonstrated excellent results as electron collector materials, leading to elevated current densities at the cathode [2]. Besides, semiconductors like $BiVO_4$ and WO_3 can serve as light absorbers and photoelectrocatalysts for the oxygen evolution reaction (OER) enhancing the harvest of solar irradiation due to an enhanced light absorption and reduced electron-hole recombination [3].

This work aims to develop and optimize a front or back-illuminated photoanode that combines $CaTiO_3$ as an electron collector layer with different ratios of WO_3 and $BiVO_4$ onto a Fluorine Doped Tin Oxide (FTO) or carbonaceous substrates for an efficient solar-driven CO_2 photoelectroreduction (PEC) to formate. Different electrode configurations are proposed, including the preparation and deposition layer by layer, physical mixing, or both.

2. Methods

Photoelectrode manufacturing was carried out using an automated spray pyrolysis technique, previously optimized for depositing materials in different layers over the FTO and carbon substrates [2]. The optimal fabrication conditions involve a spraying nozzle height of 35 mm, an ink flow rate of 20 mL min^{-1}, and a step distance of 1 mm while keeping a constant temperature of 70 ºC. The ink contains isopropanol as the solvent, the photoelectrocatalyst, and Nafion as a binder. The different catalysts are coated onto the substrates with different loadings (1-5 mg cm^{-2}) and mass ratios, which are optimized to reach the best PEC performance.

The photoactive surfaces are fully characterized using different physicochemical and (photo)electrochemical techniques, such as SEM, PXRD, as well as EIS across a range of frequencies from 10 kHz to 50 Hz and continuous chronoamperometries at a constant voltage of -1.8 V and -2 V vs.

Ag/AgCl with and without light irradiation. Subsequently, the fabricated photoanodes are evaluated in a photoanode-driven divided filter-press reactor in continuous mode under visible light irradiation (100 mW cm^{-2}), with a platinized titanium plate serving as the dark cathode and an aqueous solution of 0.5 M $KHCO_3$ as the electrolyte.

3. Results and discussion

The results on optimizing the perovskite layer show that the lowest loading (1 mg cm^{-2}) exhibits higher PEC activity, attributed to reduced particle agglomerations allowing light to reach larger active areas. Notably, a competitive current density of -71 mA cm^{-2} is achieved at -1.8 V (vs. Ag/AgCl). Preliminary tests integrating this photoanode in PEC CO_2 reduction result in a formate concentration of 63.8 g L^{-1}, thus demonstrating the competitiveness of this process [2]. Subsequently, the $BiVO_4/WO_3$ ratio is independently optimized, testing different ratios (80:20, 50:50, 20:80) with WO_3 as the bottom layer. Higher $BiVO_4$ loadings (80:20) exhibit the most favorable results in terms of photogenerated current density (0.66 mA cm^{-2}) and H_2 production (155.7 μmol m^{-2} s^{-1}), denoting an efficient electron-hole separation. Once both perovskite and $BiVO_4/WO_3$ layers are optimized, the next step covers including these materials in the same photoanode, exploring under different configurations, such as independent layers or the combination of different materials in the same matrix (physical mixture). WO_3 and $CaTiO_3$ are considered as the electron collector layers with $BiVO_4$ as the top layer for light absorption.

Finally, the PEC activity and overall energy efficiency are tested using solar light concentration techniques for an enhanced electron flow to the cathode, where the effect of increasing the irradiation intensity over the photoanode surface will be evaluated as a critical aspect to identify the most efficient configuration for scaling up the technology using sunlight.

4. Conclusions

The integration of perovskite materials in the photoanode, combined with tailoring WO_3 and $BiVO_4$ mass ratio and layers configuration is demonstrated to be a promising strategy for reducing the energy requirements for converting CO_2 into formate. Ongoing research efforts are crucial to increase PEC activity and process efficiency. Thoughtful design and optimization of photoanodes, combining the aforementioned findings, are essential to enable practical applications with PEC CO_2 reduction technology.

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Keywords

CO_2 photoelectroreduction, perovskites, $BiVO_4$, WO_3, multilayered photoanodes design.