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Perovskite-based surfaces as photoanodes for an enhanced solar-driven CO_2 reduction to formate

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The photoelectrochemical reduction of CO_2 holds promise for reducing CO_2 emissions by generating value-added products with a lower energy penalty. In this process, solar energy can provide extra electrons for CO_2 reduction at the cathode in a photoanode-based reactor configuration[1]. Although TiO_2 serves as a benchmark semiconductor, its limited absorption of visible light, primarily absorbing UV light due to its wide bandgap (3.2 eV), prompts exploration of other n-type semiconductors (e.g., ZnO, $BiVO_4$, WO_3) for a more efficient solar irradiation harvest in the water oxidation reaction [2]. Light absorption can be further enhanced by combining these semiconductors with materials like perovskites in multi-layered surfaces, facilitating charge separation and electron mobility [3]. Thus, this work aims to develop efficient photoanodes for photo-assisted CO_2 electroreduction systems capable of generating substantial photo-generated current densities at the cathode.

To achieve this, photoanodes based on a commercial calcium titanate perovskite ($CaTiO_3$) and $BiVO_4$ layers coated onto a transparent FTO substrate by automated spray pyrolysis are proposed. Different photoanode configurations are tested, with special emphasis on the materials' position (top/bottom) and illumination conditions (back/front). The most favorable results are achieved when $BiVO_4$ is positioned as the top layer with back illumination [4]. In this configuration, light reaches the transparent FTO substrate, interacting first with the $CaTiO_3$ layer, while the $BiVO_4$ is in contact with the liquid electrolyte to conduct the Oxygen Evolution Reaction. Optimizing the catalytic loading of each layer reveals an optimal loading of 1 mg cm^{-2} of $CaTiO_3$ and 3 mg cm^{-2} of $BiVO_4$, yielding an impressive current density of -71 mA cm^{-2} at -1.8 V vs. Ag/AgCl. This optimal photoanode is integrated into an electrolyzer for continuous visible light-driven CO_2 reduction in the gas phase to formate, obtaining a concentration of 63.8 g L^{-1}, with a Faradaic Efficiency of 79.1 %. These results represent a significant advancement in the development of efficient photoanode and offer advance towards future scalability of photoelectrochemical CO_2 reduction processes.

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References:

[1] J. Antonio Abarca, G. Díaz-Sainz, I. Merino-Garcia, A. Irabien, J. Albo, J. Energy Chem. 85 (2023) 455–480.

[2] S. Castro, J. Albo, A. Irabien, ACS Sustain. Chem. Eng. 6 (2018) 15877–15894.

[3] M. Passi, B. Pal, Powder. Technol. 388 (2021) 274–304.

[4] J.A. Abarca, I. Merino-Garcia, G. Díaz-Sainz, M. Perfecto-Irigaray, G. Beobide, A. Irabien, J. Albo, Catal. Today. 429 (2024) 114505.