ABSTRACT - ORAL

Solution-Processed Functional Ceramic Oxides for Solar Fuel Production: Heterojunction Photocathodes and Exsolved Photothermal Catalysts

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Functional ceramic oxides possess the chemical stability and electronic band structures required to drive solar energy conversion, under demanding conditions, into chemicals and fuels like hydrogen and valuable hydrocarbons. Applied as photo-electrodes in liquid-phase photo-electrochemical (PEC) reactors or as catalysts in gas-phase photothermal reactors, these metal oxides show potential to directly capture and store intermittent solar light into chemical bonds.

Here, we explore advanced wet-chemical processing routes – specifically neutral-pH aqueous solution-gel methods – as flexible and highly tunable strategies for producing advanced ceramic coatings and functional powders. These liquid-phase synthesis techniques grant atomic-level precursor control and excellent phase purity of the final material. Crucially, the mild nature of the pH-neutral aqueous precursors enables the precise fabrication of multi-layered ceramic heterojunction architectures, in this use case designed to optimize charge carrier extraction across semiconducting ceramic interfaces.

Multifunctional Cu-based ternary ceramic oxides exhibit potential for both PEC and plasmon-assisted catalytic solar fuel production. In the PEC route, the ternary oxide copper bismuth oxide ($CuBi_2O_4$) stands out as an attractive p-type semiconductor cathode material due to its favorable 1.85 eV bandgap. We show that homogeneous and phase-pure ceramic thin films photocathodes can be prepared through chemical solution deposition (CSD). To overcome intrinsic bulk transport limitations and surface recombination, ceramic electron- and hole-transport layers (ETL, HTL) were integrated via sequential CSD and thermal treatment, resulting in fully engineered ceramic stacks. Decorating the stack with a nanoscale Pt co-catalyst yields a near threefold increase in photocurrent density for the hydrogen evolution reaction (from $-0.10\ mA/cm^2$ to $-0.30\ mA/cm^2$ at $0.25\ V$ vs. RHE under $100\ mW/cm^2$ illumination).

In plasmon-resonance assisted photocatalytic solar fuel production, several ternary Cu-based ceramic oxides demonstrate potential as a precatalyst for the reverse water-gas shift reaction within a continuous-flow photothermal reactor. Several ceramic Cu-Nb and Cu-Fe oxides are obtained through careful selection of precursor stoichiometry and processing conditions. Combined thermal energy and illumination, under the reductive reaction conditions, trigger the exsolution of metallic Cu nanoparticles onto the surface thereby enabling the conversion of CO_2 to CO.

Overall, this work demonstrates how precision wet-chemical synthesis and interfacial engineering unlock the full potential of functional ceramic oxides for sustainable solar fuel production.