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Synthesis of transition metal doped $BiVO_4$ nano photoanodes from single source precursors

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As global energy demands, and related environmental concerns grow, there is an urgent requirement to harness alternative energy sources, such as solar energy. One attractive opportunity is to utilise sunlight to split water, forming H_2 which may be used directly as a fuel or as a reagent for the preparation of liquid fuels. $BiVO_4$ exhibits a valence band edge at a suitable position for water oxidation (2.4eV vs reversible hydrogen electrode (RHE)), and a conduction band edge located close to RHE. The band gap of $BiVO_4$ allows absorption of a significant portion of visible light, giving a theoretical Solar-to-Hydrogen (STH) efficiency of 9%. $BiVO_4$ exhibits good photostability, non-toxicity and is composed of earth abundant, non-costly elements. It occurs in three polymorphs, with the monoclinic scheelite structure as the most effective as a photoanode. However, the low carrier diffusion length (70-100nm) reduces the efficiency of photo-absorption due to accumulation and recombination of charge carriers. Efforts to remediate this issue include doping, Nano structuring, heterojunction formation. Recent reports state the necessity for simple scalable routes to deposit thin films of $BiVO_4$ onto conductive surfaces for the preparation of larger photoanodes. Simple solution preparation routes such as spray pyrolysis or drop casting/spin coating are particularly attractive due to their simplicity and potential for scale up. Current methodologies commonly use inorganic salts and/or metal organic precursors. A challenge when using a mixture of precursors is the even distribution of molecular precursors and prevention of phase separation upon the film prior to annealing. Here we report a one step, straightforward synthesis with polyoxometalates as suitable single-source precursors for nanoporous thin films of Co/Ni/Cu/Zn doped-$BiVO_4$, which show good photoactivity and can be produced on a large scale due to the simplicity of deposition.

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