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Visible light-driven catalysts for water oxidation: towards solar fuel biorefineries

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Photoelectrochemical (PEC) water splitting is a direct way of producing a solar fuel like hydrogen from water. The bottleneck of this process is the photoanode which is responsible for the water oxidation side of the reaction^{1,2}. Semiconductor metal oxides are preferred catalysts for this reaction because of their stability under oxidizing conditions and being generally low-cost. However, no single catalyst can fulfil all the requirements for an efficient water oxidation reaction. There are always trade-offs among the light-harvesting ability, the charge transport and charge transfer processes, and the catalyst's influence in the kinetics of the reaction.

In this work, the use of BiVO_4 as a photoanode was extensively studied in order to improve its photoactivity. BiVO_4 has a conduction band edge position that almost coincides with the thermodynamic hydrogen evolution potential, thus, it can promote an earlier photocurrent onset, and can generate a higher photocurrent in the low bias region compared to the other photoanodes. These properties are vital in obtaining a high overall operating current and can eventually lead to a

higher STH efficiency. In addition, BiVO_4 has a relatively low band gap energy of 2.4-2.5 eV, which makes it readily absorb visible light³. Its theoretical maximum photocurrent density is 7.5 mA/cm^2 . However, the drawbacks of using BiVO_4 photoanodes are poor electron mobility and poor water oxidation kinetics. Poor electron mobility brings about the loss of the photon efficiency to electron-hole recombination⁴. Moreover, BiVO_4 is not a good water oxidation catalyst.

The optimization of BiVO_4 photoanode synthesis via thin film electrodeposition on FTO was performed. The factors affecting the photoelectrochemical activity such as the electrodeposition time, ratio of the Bi-KI to benzoquinone-EtOH in the deposition bath, and the calcination temperature, have been investigated by using the Central Composite Design of Experiments. Pristine monoclinic scheelite BiVO_4 photoanodes having a photocurrent density of $0.45 \pm 0.05 \text{ mA/cm}^2$ at 1.23 V vs RHE have been obtained. It was shown that a high photocurrent density are generally dictated by the following physico-chemical properties: higher crystallite size, an optimal thickness, and a more compact,

porous morphology. Furthermore, the following photoelectrochemical characteristics give rise to a higher photocurrent density: low onset potential, and a high donor density.

Surface states on the BiVO₄ surface give rise to defect levels, which can mediate electron-hole recombination via the Shockley-Read-Hall mechanism⁵. In order to minimize the inefficiencies due to electron-hole recombination and passivate the surface states, ultrathin overlayers of Al₂O₃ and TiO₂ were deposited to the BiVO₄ thin film electrodes in an ALD-like manner. This was also performed in order to protect the BiVO₄ surface from photocorrosion and increase its stability. A photocurrent density of 0.54 mA/cm² at 1.23 V vs RHE was obtained for the Al₂O₃-modified BiVO₄, which was a 54% improvement from the bare BiVO₄ that demonstrated a photocurrent density of 0.35 mA/cm² at 1.23 V vs RHE. A 15% increase in stability of the Al₂O₃- modified BiVO₄ electrode was also observed over 7.5 hours of continuous irradiation. Moreover, through surface capacitance measurements, it was shown that the Al₂O₃ overlayer was indeed passivating the surface states of the BiVO₄ electrodes. The nature of the BiVO₄ surface was studied in this chapter by investigating the reactivity of powder BiVO₄ with a chemical titrant. The existence of surface hydroxyl groups on BiVO₄ was confirmed and quantified (max 1.5 OH/nm²) via chemical titration. The reaction of the BiVO₄ powder with one pulse of AlMe₃ and 1 pulse of H₂O showed that there were 1.2 molecules of CH₄ evolved per Bi-OH.

Meanwhile, there were no photocurrent density improvements that were observed for the TiO₂-modified BiVO₄ at the synthesis conditions that were used in this experiment.

The addition of Ni-Mo to bare BiVO₄ increases the photocurrent density by 3-fold, from 0.35 mA/cm² to 1 mA/cm² at 1.23 V vs RHE. This was mainly due to the much lower charge transfer resistance of this electrode with respect to bare BiVO₄. Moreover, the addition of Ni-Mo to BiVO₄ with an overlayer of 2 cycles of Al₂O₃ produces a photocurrent density (0.39 mA/cm² at 1.23 V vs RHE) that is lower than that of just BiVO₄ with Ni-Mo, and slightly higher than that of the bare BiVO₄ for potentials up to 1.3 V vs RHE. It is apparent that the charges were able to transfer more efficiently from the BiVO₄ surface to the Ni-Mo, than from the Al₂O₃ overlayer to the Ni-Mo. This very important interface needs to be further examined and optimized.

In this work, we were able to highlight which factors are important in the synthesis of BiVO₄, and how they affect the resulting photoactivity. We have also achieved the passivation of the BiVO₄ surface states using Al₂O₃, which is not well-explored in literature. Moreover, we were able to probe and discuss the nature of the BiVO₄ surface. This is a very fundamental knowledge and the first of its kind, to the best of our knowledge. A good understanding of this important semiconductor surface and its interactions will aid in the design of a more efficient BiVO₄ photoanode.