



POLITECNICO DI TORINO
Repository ISTITUZIONALE

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

Original

Visible light-driven catalysts for water oxidation: towards solar fuel biorefineries / Tolod, Kristine. - (2019 May 06), pp. 1-109.

Availability:

This version is available at: 11583/2732969 since: 2019-05-13T09:05:33Z

Publisher:

Politecnico di Torino

Published

DOI:

Terms of use:

openAccess

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)



POLITECNICO
DI TORINO



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

Kristine Rodulfo Tolod

PhD in Chemical Engineering, XXXI cycle

Supervisors: Prof. Nunzio Russo, Dr. Simelys Hernández, Dr. Elsje Alessandra Quadrelli

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.