Light assisted solar fuel production by artificial CO_2 Reduction and water Oxidation

Deliverable D3.1

Optimized $BiVO_4$ photoanodes with coupled WOC

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EXECUTIVE SUMMARY

This document is a public report that contains information about bismuth vanadate ($BiVO_4$) photoanodes with molecular water oxidation (WOC) catalysts coupled to their surfaces. Given the confidential nature of the work, the synthesis conditions and identity of the WOC are provided in general terms, more details are to be found in the confidential 18-month review report. The basic properties of the electrodes and their representative performance characteristics are described. This report is a deliverable of the LICROX Project, which is funded by the European Union's H2020 Program under Grant Agreement No. 951843. The $BiVO_4$ photoanodes with coupled water oxidation catalysts will later be integrated into the complete LICROX device and, together with the photocathode with coupled CO_2 reduction catalyst and organic photovoltaic solar cell component, will enable spontaneous overall CO_2 reduction to solar fuels.

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WP3: Semiconductors for the photoanode and cathode

By the implementation of WP3 we will target: i) The fabrication of highly efficient and stable $BiVO_4$ photoanodes as model systems that provide a basis for prototype development; ii) The development of high surface area WO_3 electron selective charge extraction layers fabricated from scalable NP dispersions; iii)The development of Fe_2TiO_5 photoanodes that overcome the fundamental limitations associated with $BiVO_4$; iv) The development of highly active and stable $CuFeO_2$ photocathodes; v) Engineering photocathode structures and interfaces to enhance CO_2R efficiency and C-C containing products selectivity; and vi) Synthesis of semiconductor NPs for an up-scalable production of photo- anodes and cathodes.

1. Purpose of the $BiVO_4$ photoanode with coupled water oxidation catalyst

The purpose of the $BiVO_4$ photoanode with coupled water oxidation catalyst is to absorb visible light as the wide bandgap top absorber of the LICROX device and to promote the oxidation of water at catalytic sites on its surface. To accomplish these tasks with reasonable efficiency, high quality films must be produced that enable effective electron-hole charge separation, photocarrier transport, and interfacial hole injection. Coupling of the molecular catalysts to the surface must be achieved using robust chemical linkages and the complete assembly must remain stable under oxidizing reaction conditions within the carbonate buffer solution used in the LICROX device.

2. Synthesis and characterization of the $BiVO_4$ photoanode

To optimize the functional characteristics of the $BiVO_4$ photoanode, several different synthesis procedures were applied and the resulting properties of the electrodes were characterized. In addition to optimizing the synthetic conditions, the role of WO_3 electron selective back contacts and the incorporation of foreign atom dopants were investigated, with an aim of increasing photocurrent densities and operational lifetimes. To provide a reasonable comparison to the literature, all electrodes were initially tested using 0.5 M KPi buffer solution with 1 M Na_2SO_3 as a sacrificial hole acceptor. The electrochemical cell was arranged in a three-electrode configuration, using a Ag/AgCl reference electrode, a Pt counter electrode, and the $BiVO_4$ as working electrode illuminated with simulated AM1.5G 1 Sun radiation.
Figure 1(a) shows the nanoscale morphology of the best performing $BiVO_4$ photoanode under the above-described electrolyte conditions. The corresponding linear sweep voltammogram (Fig. 1(b)) exhibits a photocurrent onset potential of ~0.3 V vs. RHE and a photocurrent density of >3.0 mA/cm^2 at 1.23 V vs. RHE. This photocurrent density fulfills the requirements of Milestone 3. Only a mild decline of the photocurrent was observed under continuous operation for 1 h.

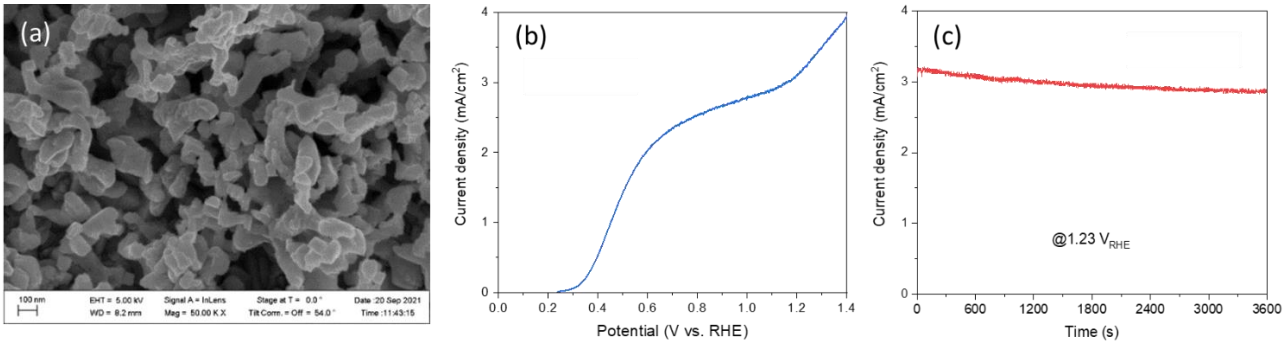

Fig. 1: (a) Scanning electron micrograph showing the nanoscale morphology of the $BiVO_4$ photoelectrode optimized for operation under KPi buffer electrolyte. (b) Linear sweep voltammogram indicates performance characteristics that fulfill the requirements of LICROX Milestone 3. (c) Chronoamperometric characterization indicated a high stability of the optimized photoelectrode during a 1 h operational test.

3. Electrochemical behavior of the bare $BiVO_4$ photoanode in carbonate buffer

In addition to benchmarking the performance of $BiVO_4$ photoanodes under a standard KPi buffer, additional optimization was performed for the operation of $BiVO_4$ under carbonate buffer. This is the electrolyte environment under which the photocathode is designed to operate and there are device-level advantages to both photoanode and photocathode operating in a common electrolyte. These experiments revealed desirable performance characteristics, even in the absence of a sacrificial hole acceptor or WOC. However, it was discovered that the nanoscale morphology of the electrode described above inhibits photocurrent in the absence of WOC, with planar electrodes offering the best combination of performance characteristics prior to WOC integration. Fig. 2(a) shows the morphology of the best-performing planar electrode, which yielded the linear sweep voltammogram in Fig. 2(b). Importantly, oxygen product analysis of this photoelectrode indicated non-unity Faradaic efficiency, highlighting the need for an integrated WOC on the surface and opportunities for further performance optimization (see below)

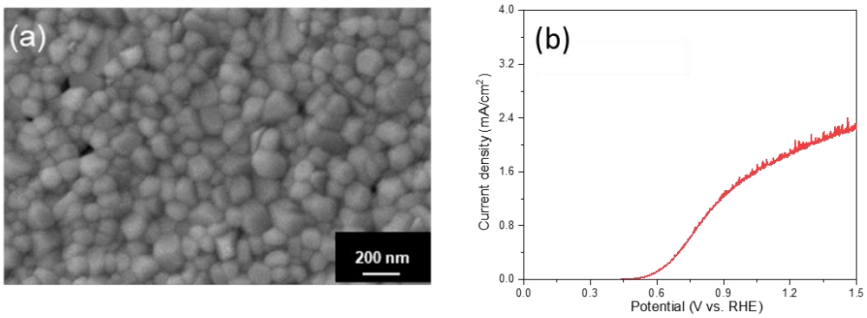

Fig. 2: (a) Scanning electron micrograph showing the nanoscale morphology of the $BiVO_4$ photoelectrode optimized for operation under carbonate buffer electrolyte prior to integration of water oxidation catalyst. (b) Linear sweep voltammogram obtained under carbonate buffer prior to integration of WOC.

4. Coupling of the WOC and evaluation of photoelectrochemical performance

Molecular water oxidation catalysts were prepared based on Ru and Fe complexes with the adequate modifications at the auxiliary ligands for their deposition into the surface of the $BiVO_4$ semiconductor under a controlled manner. The Ru complexes were modified with long alkyl chains at the polypyridyl ligands so that they could be anchored via a self-assembled bilayer strategy. On the other hand, the Fe complexes were modified using a thiophene functionality that allowed anchoring via an anodic electropolymerization. In both cases the anchoring strategy resulted in significant improvements in the photocurrents obtained when the catalyst was anchored on the semiconductor with regard to their analogues in the absence of catalyst under the same conditions.

5. Conclusions and future prospects

Having achieved the photocurrent performance milestone (Milestone 3, photocurrent density >3 mA/cm^2), we are now proceeding to combine the integrated $BiVO_4$ photoanodes together with the other device components in order to demonstrate spontaneous CO_2 reduction. This future work includes the utilization of advanced light management concepts to improve light harvesting in the $BiVO_4$ photoanode and further increase its photocurrent density. In parallel, we are examining the stability of the electrode with coupled WOC under long-term operation and are characterizing competitive reaction kinetics at the interface.