LICROX

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

Deliverable D4.2

Light absorption in the PEC

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EXECUTIVE SUMMARY

This document, a public report on the light absorption in the photoelectrochemical cell (PEC), is a deliverable of the LICROX Project funded by the European Union's H2020 Programme under Grant Agreement No. 951843. It aims to provide the reader with detailed information about the optimal PEC structure designed and fabricated to enhance absorption in the $BiVO_4$ photoanode and to balance the current among the different light absorption materials. The results from both computational simulations and experimental assembly of a half PEC are shown in this document.

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WP4: Light trapping in the PEC

In this WP4, light propagation and absorption within the photoelectrochemical cell are thoroughly studied. Computational models are implemented to optimize the PEC configuration in order to ensure an optimal light distribution throughout the whole tandem device, leading to an enhancement of the current density and of the photocatalytic performance of the PEC, as experimentally observed.

1. Purpose of light absorption studies in PECs

$BiVO_4$ is a high bandgap (about 2.4 eV) semiconductor,[1] with a much smaller absorption range than the organic photovoltaic (OPV) cell and the photocathode that compose the tandem PEC device, as demonstrated in Figure 1.

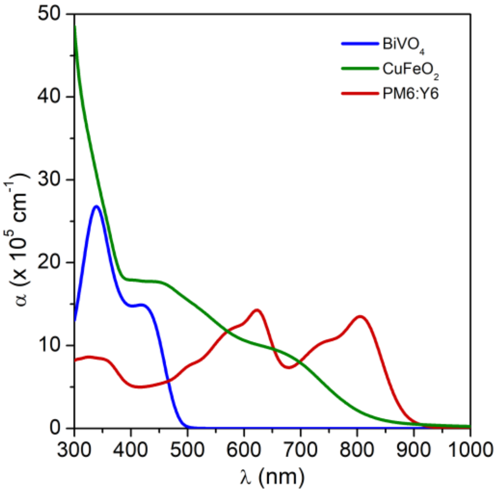

Figure 1. Comparison between the absorption coefficients of the $BiVO_4$ used as photoanode absorbing material, the PM6:Y6 blend considered for the OPV cell and the $CuFeO_2$ used as photocathode absorbing material.

For this reason, even when placing the photoanode as the front absorbing element, the current generated by it will be lower than the one produced by the other two components, which will limit the performance of the whole compact tandem device where all the elements are connected in series. This means that a large fraction of the current generated by the photovoltaic cell will not be used by the tandem, especially when a half-cell is considered.

This issue can be overcome by using 1-dimensional nanophotonic structures in between the absorbing elements to properly distribute the light within the PEC, or by introducing 3-dimensional scattering elements to improve light absorption and current density in the $BiVO_4$ photoanode. Studies of light absorption in PECs incorporating $BiVO_4$ as the photoanode active material are therefore crucial to optimize the performance of the water splitting reaction at bias-free conditions and were extensively carried out at LICROX.

In a first step, computational optimizations involving 1- and 3-dimensional systems were performed using the methods described in Deliverable D4.1 of this project. Prior to that, an optimal half-cell including a planar nanophotonic structure to manage light distribution was fabricated to validate the results of the optical simulations and to demonstrate the importance of the light absorption studies for photoelectrochemical systems.

2. Introduction of 1-dimensional structures in between the absorbing elements

To balance light distribution among the tandem elements and to enhance light absorption in the $BiVO_4$, a 1-dimensional nanophotonic structure was introduced in between the photoanode and the photovoltaic cell in a half PEC, as schematically illustrated in Figure 2. The optimal combination of materials, number of layers and thicknesses of the nanophotonic structure were theoretically found by means of an inverse design integration, performed with the objective of achieving the highest possible current density in the photoanode while ensuring that such current does not surpass the one of the OPV cell. To do so, a general transfer matrix method, used to describe the electromagnetic wave propagation, was combined with a genetic algorithm to optimize the different parameters of the photonic structure, as described in detail in Deliverable D4.1.

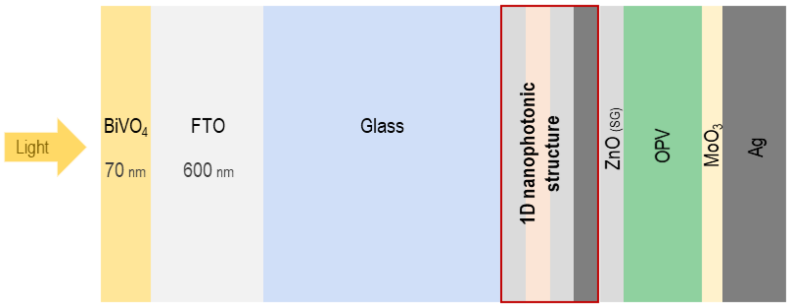

Figure 2. Planar configuration considered to optimize light distribution in a half PEC, which included a 1-dimensional nanophotonic structure in between the $BiVO_4$ photoanode and the OPV cell.

The optimal nanophotonic structures obtained from the computer simulations intercalated two different dielectric materials with contrasting refractive indexes and were finished by a semi-transparent silver layer. According to the theoretical predictions, the introduction of such structures in between the photoanode and the OPV cell allowed for an almost perfect reflection of light with low wavelengths back to the $BiVO_4$, for improved absorption, while the light with higher wavelengths continued to be transmitted to the solar cell to provide the current and voltage necessary to perform the bias-free water splitting reaction. Thanks to this optimized light distribution, a significant increase in photocurrent density was estimated when employing the 1-dimensional structures.

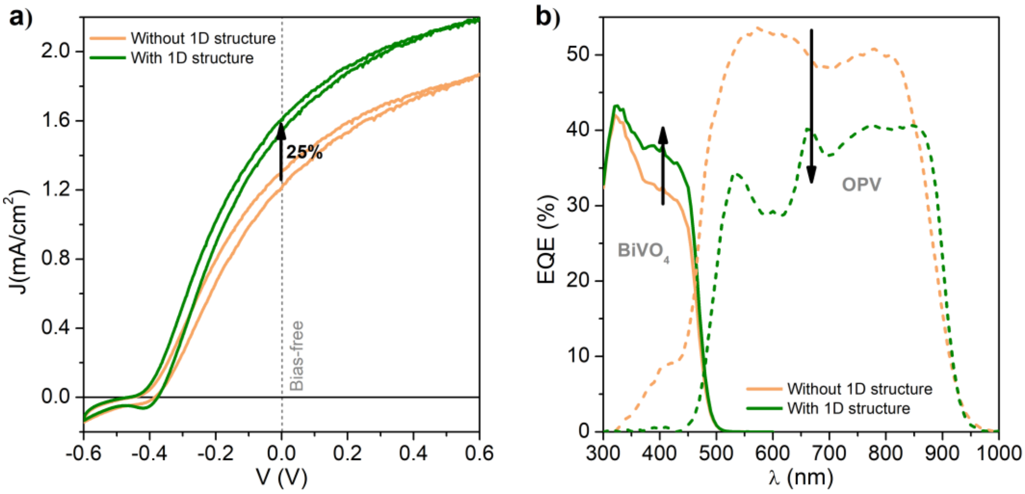

Figure 3. a) J-V characteristics of the $BiVO_4$/OPV half PEC device before and after introducing the 1-dimensional nanophotonic structure for light management. b) EQE response of the photoanode and of the solar cell at bias-free conditions with and without applying light management strategies.

D4.2. Light absorption in the PEC

In order to verify such predictions, a half PEC was experimentally fabricated using a very transparent $BiVO_4$ photoanode together with a PM6:Y6 OPV solar cell and a 1-dimensional photonic structure with optimal layer configuration.[2] When doing so, a 25% increase in bias-free current density was observed for the water splitting reaction, as illustrated in Figure 3a. EQE measurements individually performed for the photoanode and for the photovoltaic cell at bias-free conditions and presented in Figure 3b revealed a significant improvement in light distribution when the 1-dimensional structure was incorporated in the half PEC, which resulted in a substantial increase in light absorption at the $BiVO_4$, responsible for the enhanced photocurrent observed.

3. Introduction of 3-dimensional scattering elements

A different, though complementary, way of improving the performance of tandem PEC devices that use $BiVO_4$ as photoanode absorbing material consists in the introduction of scattering elements to increase the optical path, and therefore the light absorption, in the active layer without the need of thickening the $BiVO_4$, which results in significant losses due to the high recombination of charge carriers. To model such scattering effects, a 3-dimensional system must be considered, which we have done by using COMSOL Multiphysics® software, as described in Deliverable D4.1.

To get the best configurations incorporating scattering elements, a parameter sweep strategy was considered since the optimization methods previously used to solve the 1-dimensional problem are no longer adequate given the computational resources that they require. In this sense, different parameters were manually varied during the optimization process, which included: the shape and dimensions of the scatterers, their refractive indexes, the type of lattice used (square or triangular) and the periodicity. In the end, the best configurations obtained incorporated scattering elements with high refractive index and high symmetry (cylinders, cones) on top of the $BiVO_4$ layer to increase light absorption at a broad wavelength range without affecting very much the transmittance of the photoanode, as shown in Figure 4. This resulted in more than 20% increase in photocurrent density, which must be added to the one obtained by the proper management of the light distribution in the PEC cell shown in the previous section, since the transparency of the photoanode for higher wavelengths was kept practically unaltered.

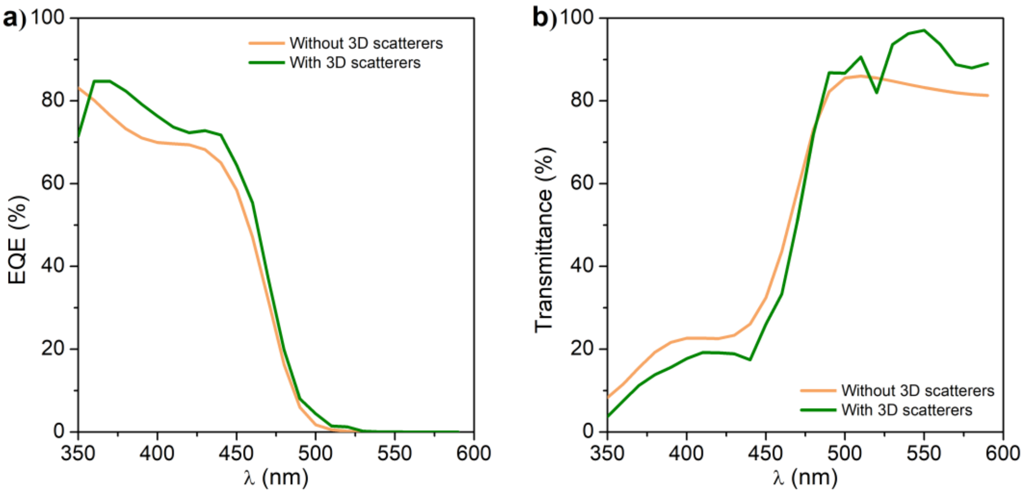

Figure 4. Simulated a) EQE and b) transmittance of the $BiVO_4$ photoanodes with and without the introduction of 3-dimensional scattering elements.

4. References

1. Cooper, J. K. *et al.* Indirect bandgap and optical properties of monoclinic bismuth vanadate. *J. Phys. Chem. C* **119**, 2969–2974 (2015).

2. Ferreira, C. G. *et al.* Bias-free solar-to-hydrogen in a $BiVO_4$/PM6:Y6 compact tandem with optimally balanced light absorption. submitted.