LICROX

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

Deliverable D5.2

Photoanode/OPV/dark cathode half-cell

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EXECUTIVE SUMMARY

This report, Photoanode/OPV/dark cathode half-cell, is a deliverable of the LICROX Project which is funded by the European Union's H2020 Program under Grant Agreement No. 951843 and contains information about the performance of the best bismuth vanadate photoanodes used in the project that are coated with molecular Cu complexes (BVO-WOC). The latter act as molecular water oxidation catalysts at neutral pH, via anodic electropolymerization of its thiophenegroup. Further, the coupling of the BVO-WOC to organic photovoltaic cells (OPV) and the performance of this hybrid ternary material (BVO-WOC-OPV) is also described. Given the confidential nature of the work, the final structures of the catalytic species and cell design are provided in general terms, more details are to be found in the confidential final review report.

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WP5. PEC implementation & validation

In WP5 the catalysts, semiconductors and light trapping strategies developed in WPs 2, 3 & 4 respectively, will be assembled together to build and test the performance of different PEC configurations. The implementation of the activities in this WP targets:

i) Assembly of the materials and optimal light trapping configurations into one single device by multi-layering or by stacking and connection through conductive materials;

ii) Assessment of the current output of the device upon simulated sun illumination; and

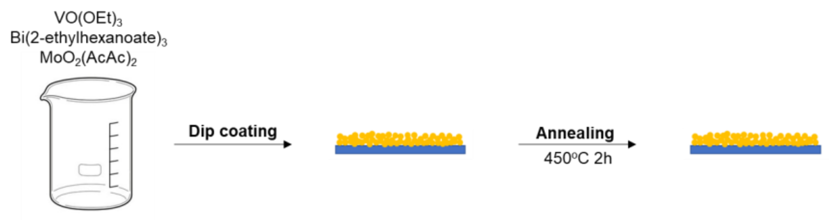
iii) Quantification of the chemical products obtained from the current output and determination of Faradaic efficiencies and solar to chemical energy efficiency.

The present report constitutes the Deliverable D5.2 Photoanode/OPV/dark cathode (Pt) half-cell, and describes the fabrication and test performance of the PEC with this configuration.

1. Preparation and performance of the BVO as light absorber

Within the LICROX project we have worked with several light absorber materials and we have selected the best ones in terms of the photocurrents generated and stability at pH 7 that turned out to be Mo-BVO and SnO_2/WO_3/BVO on an FTO substrate. The preparation of these materials is outlined in Figure 1 and involves the use $VO(OEt)_3$ as starting materials.

Mo-$BiVO_4$@FTO photoanodes



$BiVO_4$@WO_3@SnO_2@FTO photoanodes

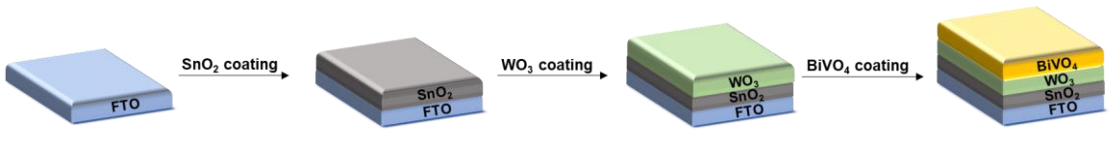


Figure 1. Scheme showing the preparation of Mo-BVO (top) and SnO_2/WO_3/BVO (bottom).

The performances of these materials at pH 7 under 1 sun light irradiation in the absence of sacrificial electron acceptors is presented in Figure 2. As can be seen in the Figure under an applied potential of 1.23 V vs. RHE (0.817 vs. NHE) the Mo-BVO and SnO_2/WO_3/BVO reach current densities in the rage of 0.2 and 1.2 mA/cm^2 respectively. The photocurrent parameters obtained here are important because they constituted the bottleneck for the coupling of the photoanode to the dark cathode for the CO_2 reduction process where current densities that are obtained are much larger.

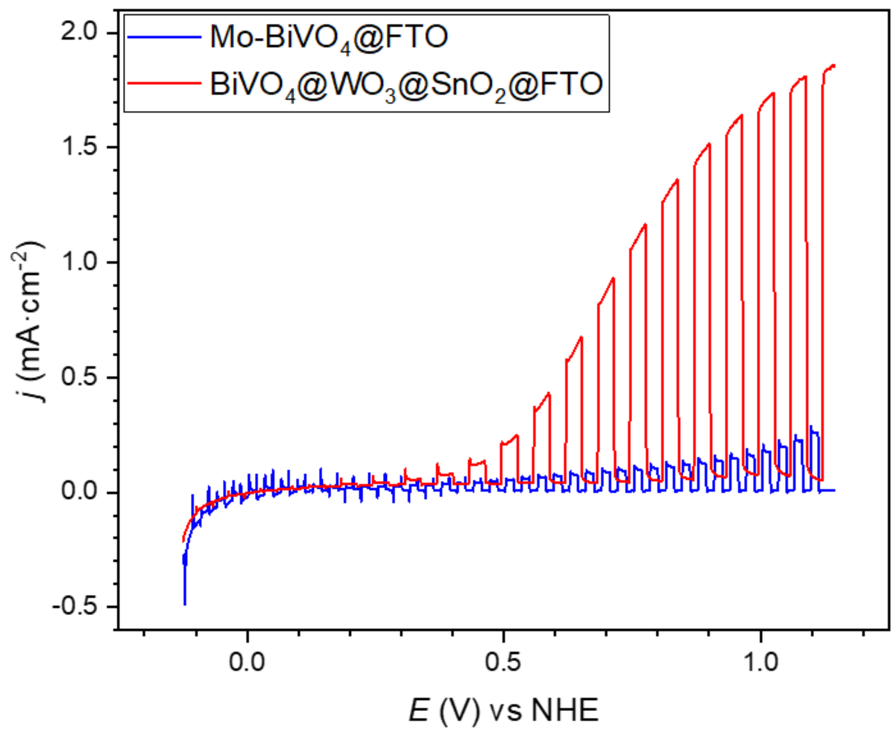


Figure 2. LSV of photoanodes under chopped light (1 sun illumination) in pH 7 phosphate buffer (I = 0.1 M). Scan rate: 20 mV/s. CE: Pt disk.

2. Building hybrid molecular materials based on BVO and molecular WOC

The next steps consisted on the deposition of the molecular catalysts developed at LICROX on the surface of the BVO. In this regard we used the tetra-amide Cu complexes[1,2] that we have described earlier and had modified with the attachment of a thiophene group at the backbone of the initial ligand (See Figure 3 onset for a drawing of the structure of this molecule). We have shown previously that under a sufficiently positive potential it generates a film of the corresponding poly-LCuII complex at the surface of a graphitic electrode.

Here the electropolymerization is carried out potentiostatically by illuminating the SnO_2/WO_3/BVO under 1 sun and while carrying out multiple CV in MeCN the current density progressively increases confirming the polymerization process is occurring.

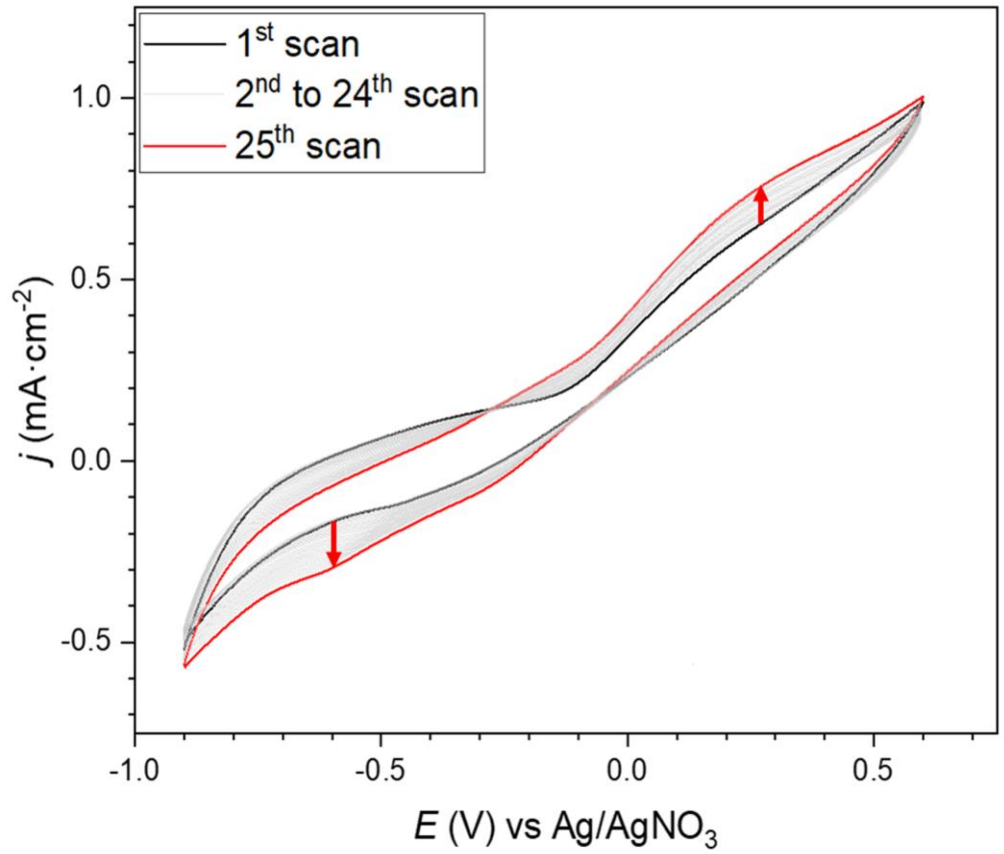


Figure 3. Photo-electropolymerization of the molecular catalysts (L-CuII; 3 mM) into SnO_2/WO_3/BVO electrode via Cyclic voltammetry (25 cycles) under 1 sun illumination. WE: $BiVO_4$. CE: Pt coil. Scan Rate: 50 mV/s. Solvent and supporting electrolyte: MeCN with 0.1 M of (NH_4)TfO (Ammonium Trifluoromethanesulfonate).

Then the electrode is rinsed with MeCN and water and introduced in a clean aqueous electrolyte pH 7 solution. As can be seen in Figure 4 there is a significant enhancement of the current density in the presence of the molecular catalyst generating a photocurrent of 1.8 mA/cm^2 at 1.23 V vs. RHE. Interestingly the stability of the material is significantly increased in the presence of the catalysts as observed by bulk electrolysis experiments and thus points out to the multiple beneficial effect of the catalysts notably: a) current density enhancement and b) long-term stability.

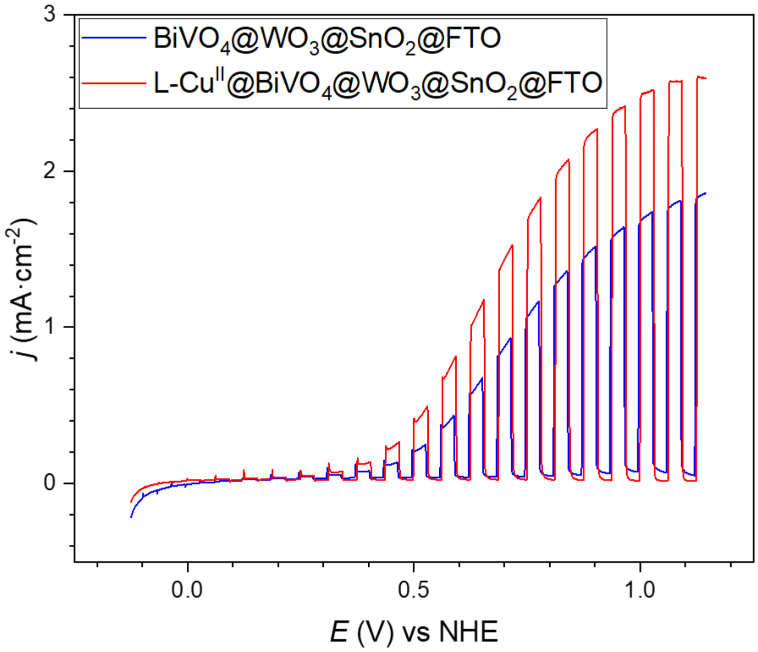


Figure 4. LSV of the photoanode before (blue line) and after (red line) electropolimerization of L-CuII. LSV recorded in pH 7 phosphate buffer (I= 0.1 M) under 1sun illumination. CE: Pt disk. Scan rate: 20 mV/s.

3. Assembling the organic photovoltaic cells into BVO-WOC and its performance

The hybrid BVO-Cu molecular material is among the best photoanodes reported up to now in terms of the photocurrents generated at pH 7 in the absence of a sacrificial electron acceptor. However, the highly negative potential needed for today's state of the art CO_2 reduction catalysts, precludes a bias-free coupling that achieve water oxidation and CO_2R in single device. In order to offset the anodic potential, we couple tandem photovoltaic cells to our best BVO-Cu at neutral pH, needed for the efficient CO2R.

4. Conclusions and future prospects

We have successfully built a highly performant device BVO-Cu/2xOPV based on the best materials developed within the LICROX project that consists of a molecular Cu water oxidation catalyst that works efficiently at pH 7, a BVO that give relatively high current densities and a 2x organic photovoltaic cell that brings 1.5 V cathodic potential offset.

This device can be coupled to the CO2R cathode and its performed is described in Deliverable D5.3

5. References

[1] M. Ventosa, M. Gil-Sepulcre, J. Benet-Buchholz, C. Gimbert-Suriñach, A. Llobet, *ACS Appl. Energy Mater*. **2021**, 4, 9, 9775–9782.

[2] P. Garrido-Barros, D. Moonshiram, M. Gil-Sepulcre, P. Pelosin, C. Gimbert-Suriñach, J. Benet-Buchholz, A. Llobet, *J. Am. Chem. Soc.* **2020**, *142*, 17434–17446.