Light assisted solar fuel production by artificial CO_2 reduction and water oxidation

Deliverable D3.2

Optimized $CuFeO_2$ Photocathodes

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EXECUTIVE SUMMARY

This document is a public report that contains information about synthesis and characterization of $CuFeO_2$ photocathodes that serve as narrow bandgap p-type light absorbers within the LICROX device. Given the confidential nature of the work, the specific synthesis conditions are discussed 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 Programme under Grant Agreement No. 951843. The $CuFeO_2$ photocathodes are developed with the aim of later integration into the complete LICROX device and, together with the photoanode with coupled water oxidation 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 optimized $CuFeO_2$ photocathode

The purpose of the $CuFeO_2$ photocathode is to absorb visible light as the narrow bandgap bottom absorber of the LICROX device and to promote the reduction of carbon dioxide to fuel products at catalytic sites on the surface. These catalytic sites are to be integrated at a later stage of the project using catalysts developed within WP2. To accomplish these tasks with reasonable efficiency, high quality films must be produced that enable effective electron-hole charge separation, photocarrier transport, and interfacial electron injection. At present, major challenges for the use of $CuFeO_2$ in solar fuels devices are short carrier transport lengths and instabilities of the surface under chemically reducing conditions. Within LICROX, approaches to overcome these challenges using new synthesis procedures of high surface area electrodes and the use of corrosion protection strategies are undertaken.

2. Synthesis and characterization of the $CuFeO_2$ photocathode

Within LICROX, two main strategies have been pursued to synthesize delafossite $CuFeO_2$ thin films. The first one is based on the more traditional sol-gel method, where molecular copper and iron precursors are mixed in solution and subsequently spin-coated on a substrate.[1] The deposited thin film is amorphous and therefore annealing at elevated temperatures is needed to obtain the desired crystalline ternary oxide. Different annealing conditions were tested in order to optimize delafossite $CuFeO_2$ films in terms of phase purity. Figure 1(a) shows the X-Ray diffraction (XRD) patterns of the thin films obtained after annealing at 700 ºC under N_2 atmosphere for different times. It is evident that longer annealing time favors the formation of higher quality delafossite $CuFeO_2$ thin films. A major hurdle that is currently being addressed is the stability of the FTO (fluorine doped tin oxide) transparent conductive oxide support during the annealing process. In particular, we have observed that the conductivity of FTO is significantly reduced under the annealing conditions that were optimized for achieving highest crystallinity and phase purity.

In parallel, we have pursued a second synthetic strategy, which is instead based on a more recent approach that exploits the solid-state reaction among nanocrystalline precursors with the advantage compared to traditional solid-state powder reactions of lowering reaction time and annealing temperature. Thus, this alternative synthetic route has potential to circumvent the hurdle associated

with thermal-degradation of the conductive support described above. Furthermore, this approach allows the formation of nanostructured thin films directly on substrates, which is not possible with traditional solid-state chemistry (i.e. traditional bulk powder-derived solid state synthesis). In this work, we have proven that the initial crystal-phase of the nanocrystal (NC) precursors plays a key role in directing the structure of the final product. Specifically, we have synthesized spinel $CuFe_2O_4$ and delafossite $CuFeO_2$ from spinel γ-Fe_2O_3 and corundum α-Fe_2O_3 NC precursors, respectively. In both cases, the Fe_2O_3 precursors were mixed with Cu NCs and annealed at 700 ºC for 30 min under inert atmosphere. Figure 1(b) summarizes the obtained results, which have been recently published.[2] The iron oxide and Cu NCs were mixed in cyclohexane and the solution was then drop-cast onto substrates. The as-obtained films were annealed to form copper iron oxide thin films. Figure 1(b) reports a schematic of the film fabrication and the XRD of the films obtained. The data reveal that (α-Fe_2O_3+Cu) NCs form the targeted delafossite $CuFeO_2$ (red trace). In contrast, the spinel $CuFe_2O_4$ (blue trace) is obtained when (γ-Fe_2O_3 NCs+Cu) NCs react.

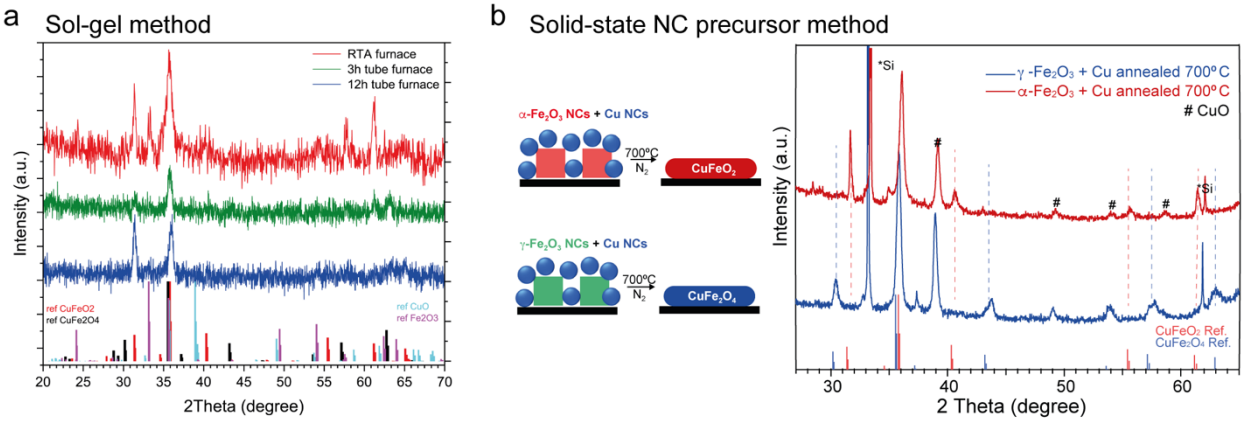

Figure 1. a) XRD patterns of the delafossite $CuFeO_2$ obtained by sol-gel method at different annealing temperature. b) Schematic and XRD patterns of the $CuFeO_2$ obtained by the solid-state reaction among nanocrystal precursors.

3. Electrochemical characteristics of the $CuFeO_2$ photocathode

The $CuFeO_2$ photocathodes were prepared on transparent conductive FTO substrates and their photoelectrochemical performance characteristics were tested in an H-type cell using CO_2-saturated 0.1M $KHCO_3$. Linear sweep voltammetry measurements under chopped 1.5 AM solar simulator light was performed to evaluate the photocurrent produced versus the applied potential (Figure 2a). The $CuFeO_2$ photocathode obtained by sol-gel method showed very poor performance showing a maximum photocurrent of -0.01 mA/cm^2, probably due to the reduction of the FTO conductivity occurring during the synthesis. On the contrary the $CuFeO_2$ photocathode obtained by the solid-state reaction among nanocrystal precursor method showed a maximum cathodic current of -1.4 mA/cm^2 (Figure 2a). The obtained photocathodes are fabricated by multiple depositions of the NC precursors, whereby we observe that thicker the photocathode higher the photocurrent. It must be noted that the maximum photocurrent possible with this method has not been achieved yet.

One of the main concerns is the instability of the $CuFeO_2$ under applied potential and light. As a mitigation plan, we are testing protection layers fabricated by atomic layer deposition. Initial results show that deposition of a Al_2O_3 layer, 20 nm thick, stabilize the $CuFeO_2$ photocurrent (Figure 2b).

However due to the insulator nature of the Al_2O_3 layer the photocurrent produced is notably reduced. Additionally, ZnO and TiO_2 or a combination of the two will be tested.[3]

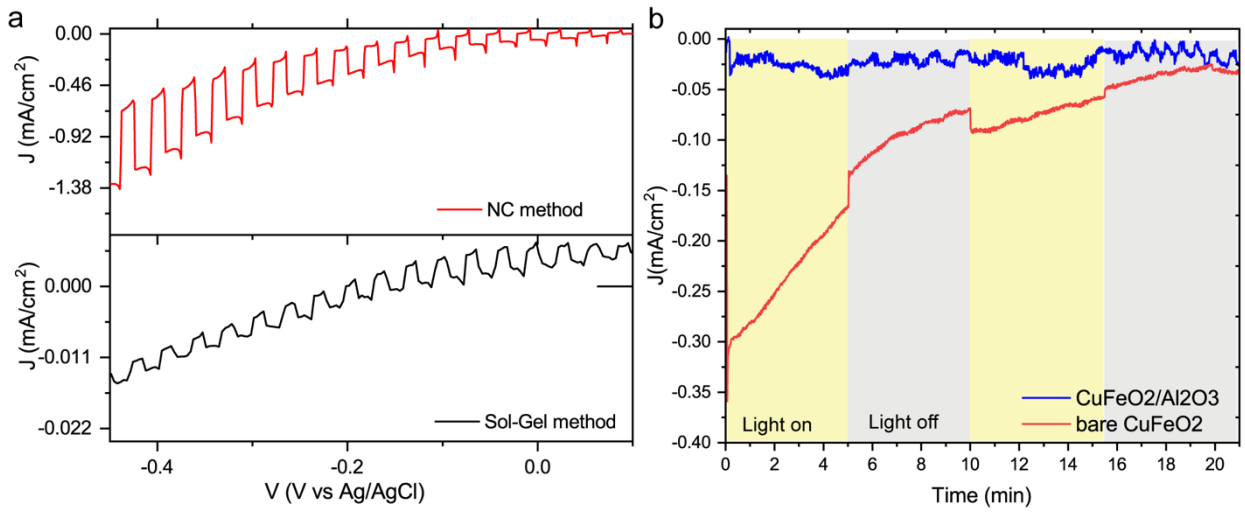

Figure 2. a) Linear sweep voltammetry of the $CuFeO_2$ film obtained by sol-gel (black curve) and NC method (red curve) under chopped 1.5AM solar simulator illumination. b) Chronoamperometry measurements performed by applying -0.4V vs Ag/AgCl in 0.1M $KHCO_3$ under chopped light for bare $CuFeO_2$ (red line) and Al_2O_3 protected $CuFeO_2$ (blue line).

4. Conclusions and future prospects

$CuFeO_2$ photocathodes able to produce a cathodic current of -1.4 mA/cm^2 have been fabricated. We are now trying to reach the highest possible photocurrent by further increasing the light absorber thickness and by improving the deposition method. One of the crucial points that has emerged is the $CuFeO_2$ photocathode stability. We are now developing the proper protecting layer that will allow to increase both stability and performance of the photocathode.

5. References

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