



Light assisted solar fuel production by artificial CO<sub>2</sub> Reduction and water Oxidation

### **Deliverable D2.3**

Tandem catalytic system for CO<sub>2</sub>R

Lead Beneficiary:	EPFL
Work Package:	WP2
Delivery date:	31 August 2022
Type of deliverable:	Report
Dissemination level:	Public
Version:	v 1.0



This Project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 951843

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### Document Information

Grant Agreement Number	951843
Acronym	LICROX
Start date of the project (Duration)	01/09/2020 (36 months)
Document due date	31/08/2022
Submission date	31/08/2022
Authors	Min Wang and Raffaella Buonsanti
Deliverable number	D2.3
Deliverable name	Tandem catalytic system for CO <sub>2</sub> R
WP	WP2 – CO <sub>2</sub> R tandem catalysis and WOC

Version	Date	Author	Description
v.0	15/08/2022	Min Wang (EPFL) and Raffaella Buonsanti (EPFL)	Creation of the first draft
v. 0.1	15/08/2022	Antoni Llobet (ICIQ)	Review
v. 1.0	30/08/2022	Laura López (ICIQ)	Final document following final revision and approval by the Project Management Board

## EXECUTIVE SUMMARY

This public report, Tandem catalytic system for CO<sub>2</sub>R, is a deliverable of the LICROX Project which is funded by the European Union's H2020 Programme under Grant Agreement No. 951843 and contains information about the synthesis and electrocatalytic testing of hybrid systems comprising Co and Fe molecular complexes and Cu nanocrystals. One manuscript is currently under peer-review and a second one is under preparation. Given the confidential nature of the work described, here we will describe the results without providing details on the nature of the molecules, more details are to be found in the confidential final review report.

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## D2.3 Tandem catalytic system for CO<sub>2</sub>R

### WP2: CO<sub>2</sub>R Tandem Catalysis and WOC

The role of WP2 is to implement the preparation of efficient catalysts that will perform the chemical reaction associated with the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) to yield solar fuels and in combination with the WOC to give oxygen gas in order to achieve high catalytic rates (high currents) and low working voltages.

#### 1. Purpose of the tandem catalytic system for CO<sub>2</sub>R (D2.3)

LICROX's final goal is the fabrication of a compact photoelectrochemical Cell (PEC) device for the production of reduced carbon products of 2 carbon atoms from CO<sub>2</sub>, such as ethylene and ethanol. Cu is the only metal catalyst which efficiently generates C<sub>2</sub><sup>+</sup> products. Yet, further selectivity enhancement and reduced overpotential are important towards technological implementation of CO<sub>2</sub>R. An ethylene selectivity above 90% at current densities  $j = 20\text{-}30 \text{ mA/cm}^2$  and onset potentials of  $E = -0.25$  to  $-0.5 \text{ V vs. RHE}$  were set as ideal for the LICROX's device.

Copper-based tandem schemes, where Cu is coupled with a CO-generating catalyst, are one of the strategies to promote the formation of multi-carbon products of CO<sub>2</sub>R. LICROX's approach was to realize tandem catalysts including Cu nanocrystals in the shape of cubes (Cu<sub>cub</sub>), which were demonstrated to be highly selective towards ethylene among all other CO<sub>2</sub>R products.<sup>[1]</sup> Because of their intrinsic tunability, we proposed molecular complexes (molCAT) as candidates for the role of CO evolving component in tandem catalysts with the Cu<sub>cub</sub> (molCAT@Cu<sub>cub</sub>).

Over the past two years, first we learned about the importance of interface sharing between the molCAT and the Cu<sub>cub</sub> to generate a bigger enhancement in the production of ethylene.<sup>[2]</sup> This work was conducted with a commercial Co-molCAT. Second, keeping this principle in mind, we combined the Cu<sub>cub</sub> with a series of Fe-molCAT, where the ligands were designed to tune the CO turnover frequency (TOF<sub>CO</sub>).<sup>[3]</sup> The most efficient Fe-molCAT@Cu<sub>cub</sub> tandem catalyst was the one including the molCAT with the highest TOF<sub>CO</sub> (0.26 s<sup>-1</sup> at -1.05 V vs RHE). This tandem catalyst exhibited a nearly 22-fold increase in the ethylene selectivity and 100 mV positive shift of the onset potential with respect to the pristine Cu<sub>cub</sub>. Specifically, ethylene was produced at a potential as low as -0.65 V vs. RHE and a selectivity of 36% at -1.05 V vs. RHE was reached, versus one of 19% of the pristine Cu<sub>cub</sub> under the exact same operating conditions.

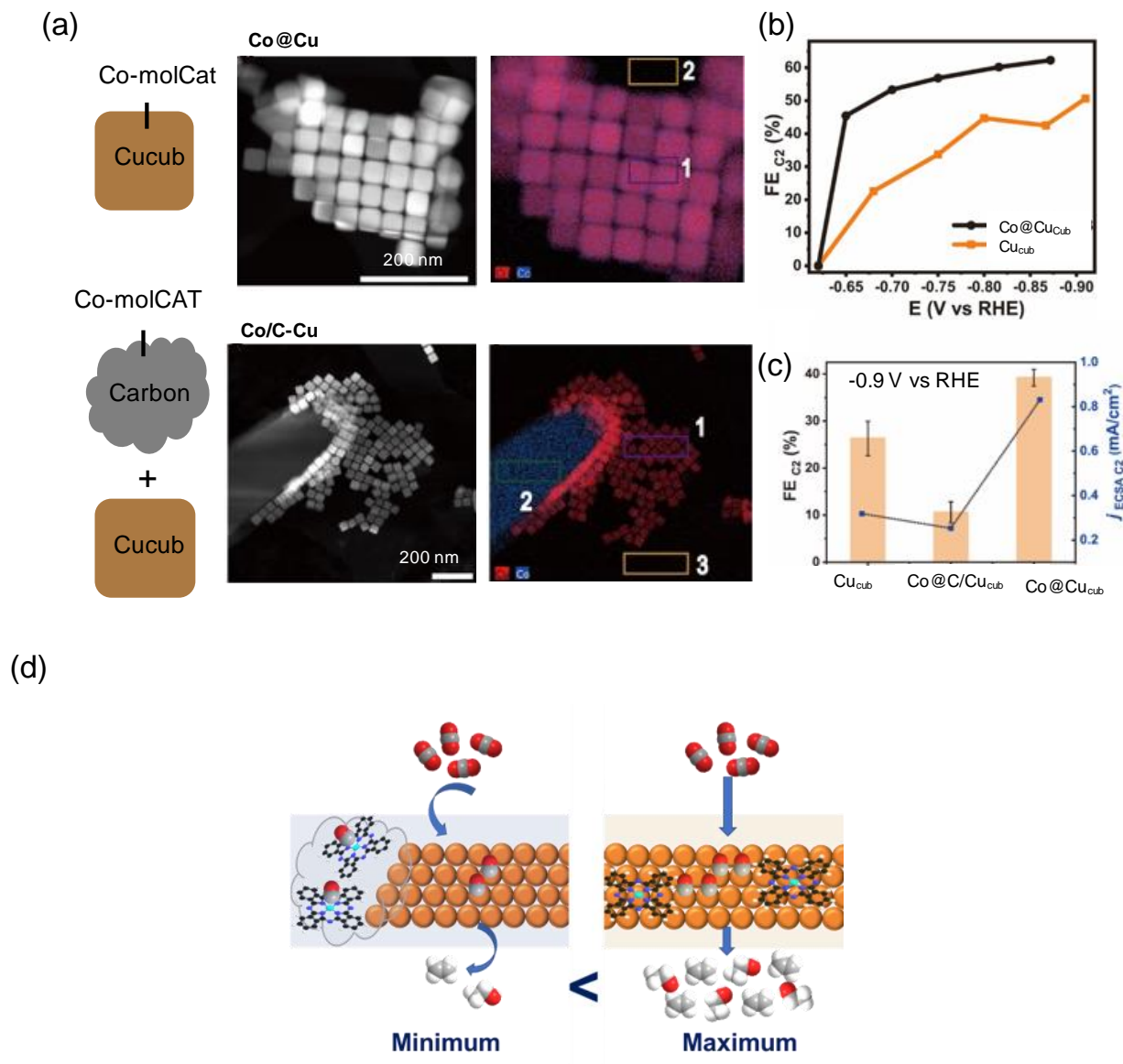
While not reported in this public deliverable, we also obtained promising results towards the aforementioned ideal ethylene selectivity and onset potential by grafting the molCAT onto the Cu<sub>cub</sub> and integrating them in a gas-fed electrochemical cell.

#### 2. About the importance of the interface in coupling Cu<sub>cub</sub> and molCAT for CO<sub>2</sub>R tandem catalysis

The first class of tandem catalysts were prepared by combining commercially available Co-molCAT and the Cu nano-cubes (Cu<sub>cub</sub>). Two approaches were followed for the synthesis: 1) depositing the molCat directly on the Cu<sub>cub</sub> (Co@Cu<sub>cub</sub>) and 2) physically mixing carbon-supported molCat with the Cu<sub>cub</sub> (Co@C-Cu<sub>cub</sub>). Figure 1 provides a summary of the most relevant results. Figure 1a reports the HAADF-STEM images along with the EDXS mapping of the two catalysts, which evidences co-location of the Co and Cu in Co@Cu<sub>cub</sub> and spatial separation of the two metals in Co@C-Cu<sub>cub</sub>. The electrocatalytic performance with optimized amounts of the two catalysts compared with bare Cu<sub>cub</sub> evidenced much higher ethylene production in the Co@Cu<sub>cub</sub> compared to the Cu<sub>cub</sub> (Figure 1b, c), under the chosen operating conditions. The superior performance of the

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Co@Cu<sub>cub</sub> was attributed to a combination of tandem and electronic effects (confirmed by XPS) promoting C-C coupling. Figure 1d reports a schematic summary of the lessons learned from this study.



**Figure 1.** (a) HAADF-STEM images (left) and EDXS elemental mappings of Cu (red) and Co (blue) for Co-molCAT@Cu<sub>cub</sub> and Co-molCAT@C-Cu; (b) Faradaic efficiency for C<sub>2</sub> products of the Co-molCAT@Cu<sub>cub</sub> and Cu<sub>cub</sub> measured at different potentials in a H-type cell in 0.1M KHCO<sub>3</sub>; (c) Faradaic efficiency and partial current density for C<sub>2</sub> products on the different catalysts measured at -0.9 V vs RHE. (d) Schematic summary

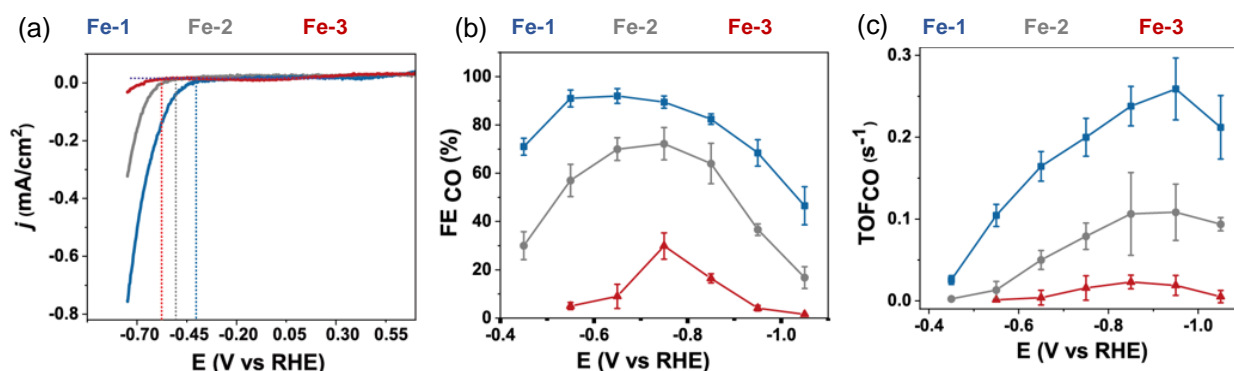
### 3. About the importance of tuning the CO-evolving properties of the molCAT to maximize ethylene production of the Cu<sub>cub</sub>

The second class of tandem catalysts were prepared by combining Fe-molCAT synthesized within the consortium and the Cu nano-cubes (Cu<sub>cub</sub>). Figures 2 and 3 provide a summary of the Fe-molCat and Fe-molCat@Cu<sub>cub</sub> electrocatalytic behavior, respectively.

We investigated the CO<sub>2</sub>R properties of the Fe-molCAT synthesized with three different ligands in an H-cell using CO<sub>2</sub> saturated and 0.1 M KHCO<sub>3</sub> as the electrolyte. Linear sweep voltammetry

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(LSV) (Figure 2a) revealed an anodic shift of the onset potential for CO<sub>2</sub> reduction from -0.57 V (Fe-3) to -0.50 V (Fe-2) and to -0.40 V (Fe-1) vs. RHE (Reversible Hydrogen Electrode). This anodic shift followed the  $\pi$ -delocalization trend induced by the ligands on the Fe-molCAT. Furthermore, the Faradaic efficiency for CO (FE<sub>CO</sub>) was higher for Fe-1 than for either Fe-2 or Fe-3 across the entire potential range (Figure 2b), with a maximum of 91% at -0.55 V vs. RHE. The TOF<sub>CO</sub> followed the same trend, with TOF<sub>CO</sub> (Fe-1) > TOF<sub>CO</sub> (Fe-2) > TOF<sub>CO</sub> (Fe-3) (Figure 2c). Specifically, Fe-1 exhibited the highest TOF<sub>CO</sub> (0.26 s<sup>-1</sup>) compared to Fe-2 (0.11 s<sup>-1</sup>) and Fe-3 (0.02 s<sup>-1</sup>) at -0.95 V vs. RHE.

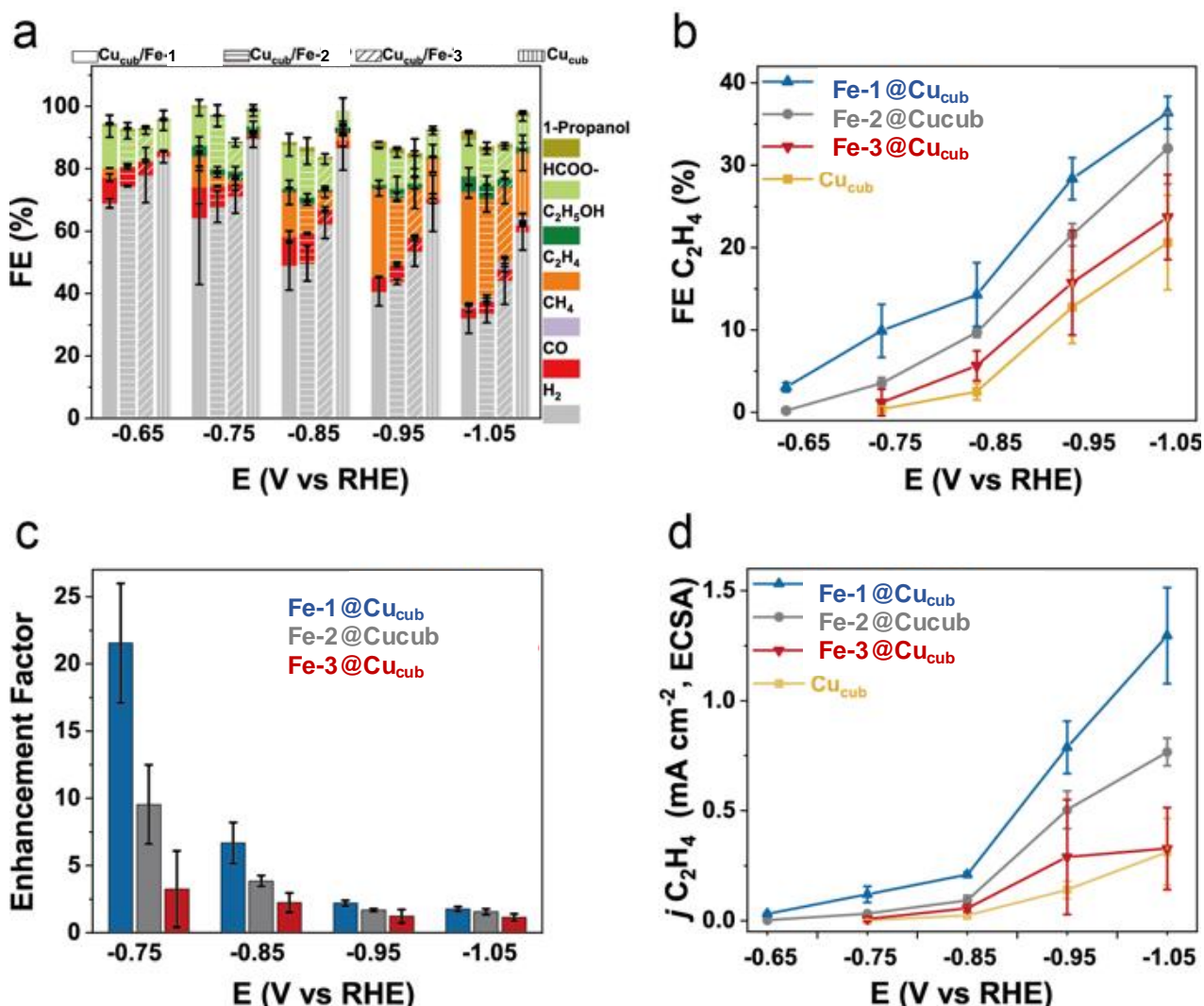


**Figure 2.** (a) LSV curves of the Fe-molCat catalysts measured at a scan rate of 10 mV s<sup>-1</sup>, with the vertical dashed lines representing the onset potentials for each catalyst; (b) FE<sub>CO</sub> and (c) TOF<sub>CO</sub> as a function of applied potential. These measurements were performed in an H-cell with CO<sub>2</sub> saturated 0.1 M KHCO<sub>3</sub> electrolyte.

Following this analysis, we prepared the Fe-molCAT@Cu<sub>cub</sub> tandem catalysts. Figure 3 provides an overview of the obtained data. At low potentials (-0.45 V and -0.55 V vs. RHE), the addition of the Fe-molCAT to Cu<sub>cub</sub> suppressed the hydrogen evolution reaction (HER) and enhanced the production of CO and formate. However, no evidence of C-C coupling reactions was observed at these potentials. The HER suppression and CO<sub>2</sub>RR promotion induced by the Fe-molCAT became more pronounced at more negative potentials (-0.65 V to -1.05 V vs. RHE, Figure 3a). Indeed, the enhancement of C<sub>2</sub>H<sub>4</sub> faradaic efficiency from Fe-molCAT@Cu<sub>cub</sub> relative to Cu<sub>cub</sub> was clearly observed for all tandem assemblies (Figure 3b). Interestingly, C<sub>2</sub>H<sub>4</sub> was produced at a potential as low as -0.65 V vs. RHE for the Cu<sub>cub</sub>/Fe-1, which maintained the highest FE<sub>C<sub>2</sub>H<sub>4</sub></sub> across the entire potential range (Figure 3b), reaching a FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of 36% at -1.05 V vs. RHE. By comparison, the Cu<sub>cub</sub> in the absence of Fe-molCAT only achieved a FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of 19% at the same potential.

To quantify the impact of the tandem catalyst assembly on C-C coupling, we defined an enhancement factor for C<sub>2</sub>H<sub>4</sub> production as the ratio of FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of Fe-molCAT to the FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of Cu<sub>cub</sub> at a given potential. The corresponding enhancement factors for Cu/Fe-1, Cu/Fe-2 and Cu/Fe-3 were 21.5, 9.5 and 3.2 at -0.75 V vs. RHE, respectively (Figure 4c). Analysis of the electrochemically active surface area (ECSA) of Fe-molCAT@Cu<sub>cub</sub> revealed a decreased solid/liquid contact area compared to the Cu<sub>cub</sub>, which is likely a consequence of the blocking of Cu active sites by the molecules. However, the ECSA-normalized current density ( $j_{C_2H_4/ECSA}$ ) indicated an increase in the intrinsic activity of the unpassivated sites in the presence of the Fe-Por, with a trend that is consistent with the FE and the enhancement factor (Figure 3d).

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**Figure 3.** (a) Total FEs and (b)  $FE_{C_2H_4}$  for tandem catalysts and the  $Cu_{cub}$  as a function of potential; (c)  $C_2H_4$  product enhancement factor of the tandem catalysts compared to the pristine  $Cu_{cub}$  (Enhancement Factor =  $(FE_{C_2H_4} \text{ of tandem catalyst}) / (FE_{C_2H_4} \text{ of } Cu_{cub})$ ) as a function of potential; (d)  $j_{C_2H_4}/ECSA$  for the tandem catalysts and  $Cu_{cub}$  as a function of potential. These measurements were performed in an H-cell with  $CO_2$  saturated, 0.1 M  $KHCO_3$  electrolyte.

## 4. Conclusions and future prospects

First of all, we learned about the importance of the preparation method and of creating interfaces between the two components.

Second, we established that the extent of the C-C coupling enhancement, as well as the anodic shift of onset potential, is directly correlated with the molCAT CO selectivity and conversion rates, which need to properly match the potential range of C-C coupling of the  $Cu_{cub}$ .

Moving forward, we demonstrated that coupling the molecular tunability of homogeneous catalysts with well-defined Cu catalysts is a promising strategy to improve the selectivity towards multi-carbon products. One of the bottlenecks that emerged is the blocking of Cu active sites by the molecular component of the tandem assembly. On the one hand, tight coupling of the organic and inorganic component is desired for ensuring efficient transport of CO to the Cu surface (whether by diffusion in the electrolyte or spillover) but this comes at cost of active site blocking. Molecular design for controlled interactions between these constituents, beyond ink formulation, would be an

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interesting path forward. The indications for Cu morphological stabilization would also be interesting to pursue further.

## 5. References

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