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

## Deliverable D2.1

# Report on Copper Nanocrystals with Different Sizes and Shapes for Selective Electrochemical $CO_2$ Reduction

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## D2.1. Nanocatalysts for CO2R

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## EXECUTIVE SUMMARY

This document is a report that contains information about copper nanocrystals with different shapes for selective electrochemical $CO_2$ reduction, it is a deliverable of the LICROX Project, which is funded by the European Union's H2020 Programme under Grant Agreement No. 951843. Tailoring copper nanocrystals towards $CO_2$ to $C_1$ and $C_{2+}$ conversion is exploited in this document. By colloidal chemistry, we successfully control the Cu shapes (cube or octahedra) with different capping ligands to reveal facet-dependent selectivity and activity trends for $CO_2$ reduction.

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## WP2: CO2R 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 $CO_2$ reduction reaction (CO2RR) to yield solar fuels and the WOC to give oxygen gas in order to achieve high catalytic rates (high currents) and low working voltages.

## 1. Purpose of the Nanocatalysts for $CO_2$ reduction

Copper (Cu) is the unique non-noble metal that can reduce $CO_2$ into $C_1$ or $C_{2+}$ molecules capable of storing chemical energy. But at this moment, selectivity and activity of polycrystalline Cu is still limited. Active research has been pursued in studying relations between nanocrystals' structure and catalytic performance, but Cu structure remains a relatively underexplored area in $CO_2$ reduction catalysis. With the purpose of making Cu more active and selective, we choose a colloidal method to synthesize and control the Cu shapes with different facets exposed by playing with the varied capping ligands. Thus, shape controlling of Cu explains how facets dependence can obtain notable changes in the electrochemical catalysis reaction.

## 2. The Cu nano-cube catalysts for $CO_2$ reduction catalysis

Our previous work has revealed a unique shape and size-dependent selectivity: 44 nm Cu cubes enclosed by {100} facets have the highest activity for $CO_2$ reduction reaction and $C_2H_4$ product selectivities.[1]

Here, Cu cubes with 44 nm (Fig. 1 a) are reproduced by the same colloidal approach. They were synthesized according to as it follows: Trioctylphosphine oxide (TOPO, 9.3728 g) was first mixed with oleylamine (OLAM, 117 mL) in a three-necked flask and the mixture was degassed for 30 min under vacuum and vigorous stirring at 120 °C then cooled down to room temperature naturally. CuBr (5 mmol) was then quickly added into the mixture under a protective atmosphere of $N_2$. The resulting solution was rapidly heated to 260 °C and held at reflux at this temperature for 1 h. The obtained Cu NCs were washed with 40 mL of anhydrous hexane by centrifugation at 6000 rpm for 10 min. The precipitated NCs were re-dispersed in 5 mL of anhydrous hexane and an equal volume of ethanol to repeat the washing. The NCs were finally dispersed in a toluene solution and stored in a glove box.

Before the electrochemical testing, there is a need to remove the native ligands to avoid possible interference with the catalytic activity. Mild-solvent washing method is effective to remove the binding organic ligands off the surface. After 3 times acetone washing and confirmed by FT-IR (*Fig. 1b*), most of TOPO ligand was desorbed without undesirable modifications of the catalysts.

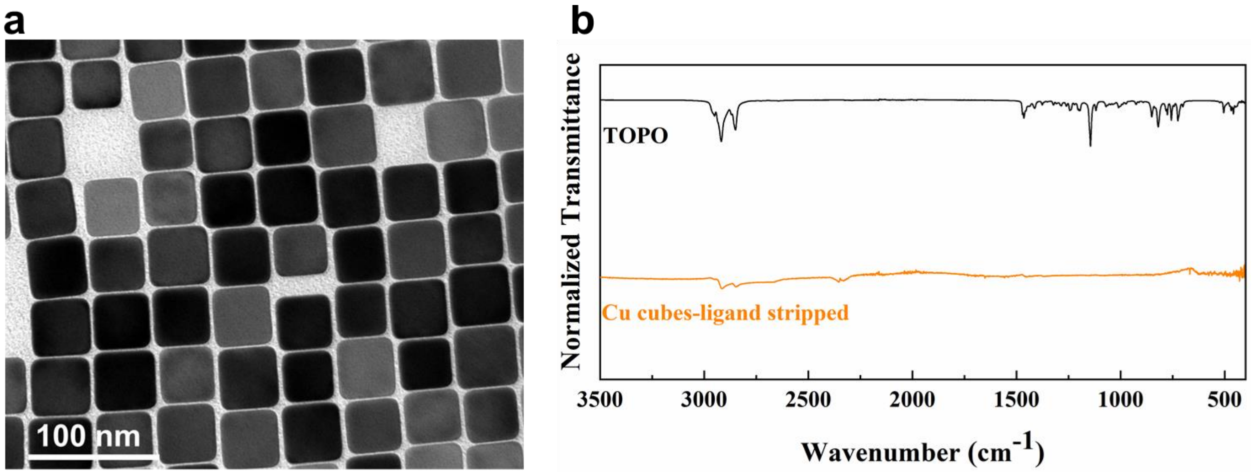

Figure 1. TEM image of Cu cubes with an average length of 44 nm (a) and FT-IR spectra of TOPO ligand and ligand-stripped Cu NCs measured as a film (b).

Electrochemical $CO_2$RRperformance was first tested in an H-type cell using $CO_2$-saturated 0.1M $KHCO_3$ at different potentials (Fig. 2 a). At -1.05 V vs RHE, Cu cubes exhibited the highest selectivity and faradaic efficiency for $C_2H_4$ (~30%). We also evaluated the $CO_2$RR performance of the Cu catalyst in the electrochemical flow cell system with a gas diffusion electrode (GDE) and employing 1 M aqueous $KHCO_3$ as the electrolyte under commercially relevant current densities (*Fig. 2b*). It shows the higher faradaic efficiencies toward the $CO_2$ reduction products while the hydrogen reduction reaction was suppressed compared to the conventional H cell. Cu cubes reach a $C_2H_4$ selectivity up to 45% at 250 mA/cm$^2$ with a mass loading of 350 µg/cm$^2$.

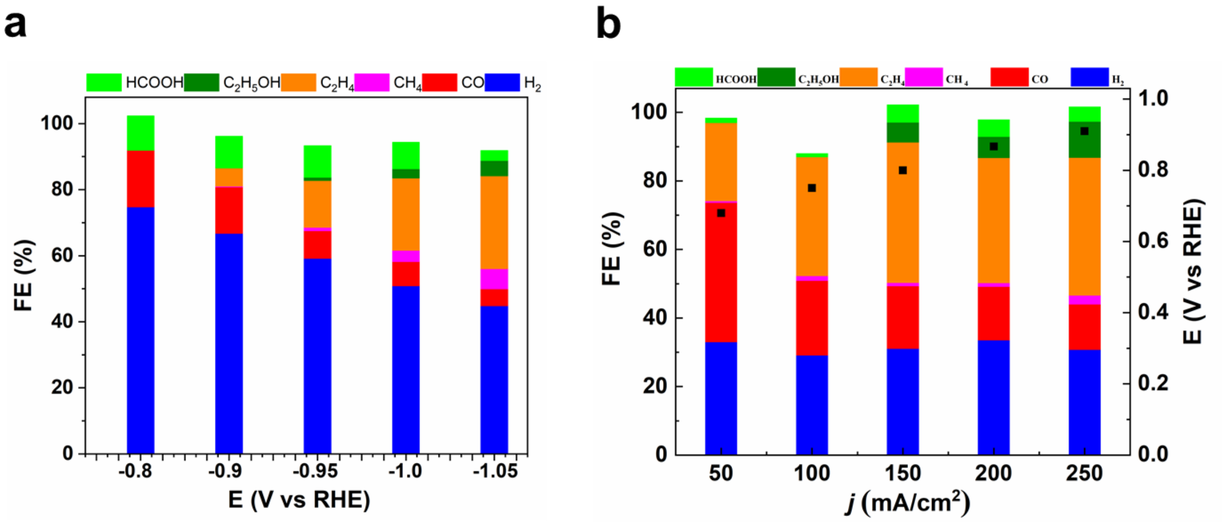

Figure 2. FEs of the Cu Cubes with a loading of 20 µg cm$^{-2}$ on glassy carbon plates (a) in H-cell and 350 µg cm$^{-2}$ on carbon paper (b) in flow cell at different potentials.

## 3. The Cu nano-octahedra catalysts for $CO_2$ reduction catalysis

To explore the structural sensitivity of the $CO_2$RR on single crystal Cu, octahedral Cu nanocrystals (Oh-NCs) enclosed by {111} facets in the range of 75–310 nm were also synthesized.[2]

The Cu Oh catalysts are shown in *Fig. 3a*. Cu nanooctahedra (75.0 nm) were synthesized following a procedure modified from literature.[3] CuBr (6.4 mmol), TOP (8.0 mmol) and olelyamine (360 mmol) were mixed in three-neck round-bottom flask (250 ml) in a glovebox before the flask was connected to a Schlenk line. After 60 mins of the nitrogen flow at room-temperature and then at $80^{o}$C, the reaction was heated to $270^{o}$C and kept for 1 hour. After this, the reaction was allowed to cool naturally and the sample was centrifuged with toluene 2 times at 6000 rpm before being re-dispersed and stored in toluene.

We found that the best way to clean the Oh-NCs surface was using $N_2$ plasma, ligands were removed after the treatment. This treatment is performed upon deposition of the NCs on a substrate (glassy carbon or silicon wafer in our case), followed by washing with ethanol to remove carbon residues.

Furthermore, to gain insight into shape-dependent selectivity and activity for $CO_2$RR, electrolysis measurements were performed in an H-type cell using $CO_2$-saturated 0.1M $KHCO_3$ at different potentials. As shown in *Fig. 2b*, among the $CO_2$RR products, $CH_4$ is favored over $C_2H_4$ along all potentials with the HCOOH selectivity decreasing when the overpotential is more negative. The best performance is achieved by the Oh-NCs with 70% FE towards the $CO_2$RR and 50% FE for $CH_4$ at -1.3 V vs RHE.

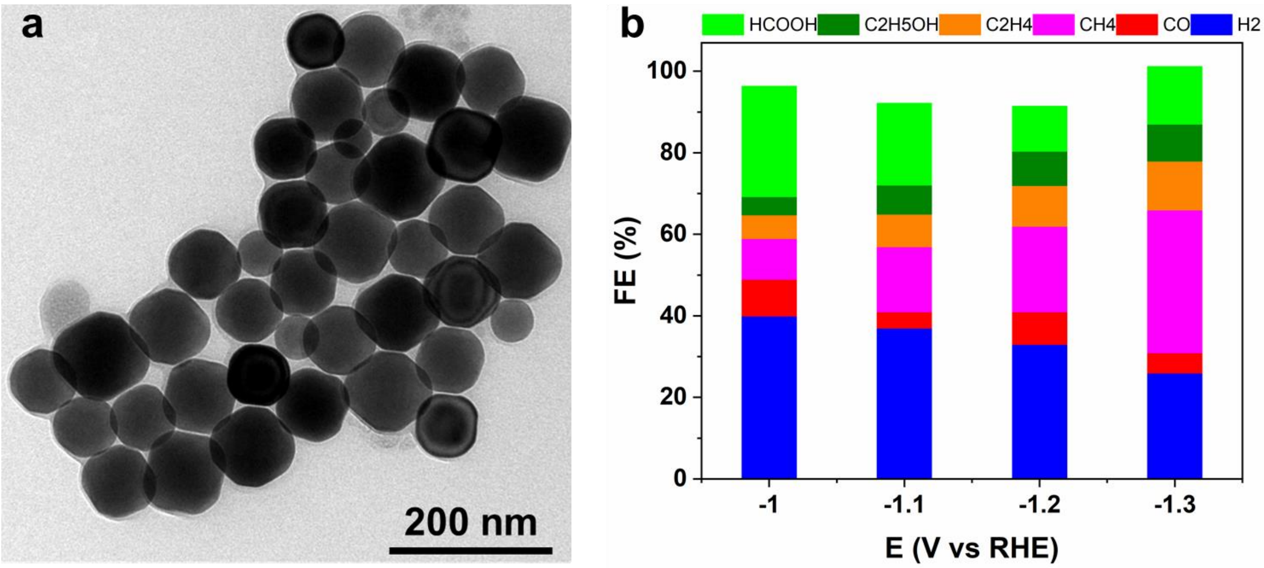

Figure 3. (a) TEM images of the 75 nm Cu Oh-NCs. (b) FEs of the Cu Oh-NCs with a loading of 20 mg $cm^{-2}$ on glassy carbon plates in H-cell at different potentials.

## 4. Main results

Catalysts in the form of copper nanocubes and octahedra have been successfully synthesized. Both catalysts have been tested in a liquid cell to prove that the nanocubes are selective for ethylene and the octahedra for methane. According to LICROX goal, the ethylene selective catalysts have been tested at higher current densities in a gas-fed cell. Selectivity for ethyelen up to 45% at 250 $mA/cm^2$ has been achieved.

## 5. Conclusions

Having assessed the intrinsic selectivity of the as-synthesized catalysts, we are now moving forward to their combination with molecular catalysts to explore tandem schemes.

## 6. References

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