

# Design of nanostructured Cu oxides for the electrocatalytic CO<sub>2</sub> reduction

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### Significance and Relevance

In the present study, Cu oxides-based materials, selected for their strong coordination ability with CO intermediates, were synthesized following different soft-chemistry approaches, varying the final morphology (*i.e.*, size/shape, aspect ratio, crystal planes orientation). After performing morphological (SEM), and structural (XRD) characterizations, such materials were thus tested in the electrocatalytic  $CO_2$  reduction (e- $CO_2R$ ), showing a different selectivity toward specific  $C_1$ - $C_2$ + products depending on the final morphology.

## Preferred and 2<sup>nd</sup> choice for the topic:

- CO<sub>2</sub> utilization and recycling.
- Fundamental advances in understanding catalysis.

Preferred presentation: Oral preferred or Short Oral

### **Introduction and Motivations**

The current energetic paradigm is based on the consumption of fossil fuels to produce energy. However, the extensive use of traditional fossil fuels is one of the major causes of the release of greenhouse gases (*e.g.*, CO<sub>2</sub>) in the atmosphere with consequent threat to the global climate balance and depletion of fossil fuels resources. Among the different alternative solution, electrochemistry is a very promising and appealing technology potentially able to accomplish the conversion of renewable sources into fuels for energy applications in a green way, alternative to the traditional fossil fuels, such as the CO<sub>2</sub> reduction (CO<sub>2</sub>R) into valuable C<sub>1</sub>-C<sub>2+</sub> products. However, the possibility of exploiting these catalytic routes to produce fuels at large scale is still strongly affected by the selection of the best catalysts and the optimization of the process parameters.<sup>1,2</sup>

### **Materials and Methods**

CuO systems were synthesized applying either a hydrothermal (H1) or a co-precipitation route (P2). Route H1: CuO formation occurred by using an alkaline solution of 6 M NaOH as precipitating agent. The synthesis took place in an autoclave by varying the treatment temperature between 150 °C and 200 °C, in a time interval of 10 hours. Route P2: synthesis took place at constant temperature (80 °C), by varying both the concentration of the precipitating agent NaOH (*i.e.*, 0.50 M, 0.75 M, 1.00 M, and 2.00 M), and the reaction time (either 30 minutes, or 2 hours).

Cu<sub>2</sub>O systems were synthesized following a selected protocol involving the precipitation of Cu<sub>2</sub>O in presence of PEG, L-ascorbic acid as reducing agent, and NaOH as precipitating agent.<sup>3</sup> Different parameters (*e.g.*, stirring time, temperature, amount of reducing agent) were systematically optimized.

### **Results and Discussion**

The following three main CuO catalysts were investigated in the e-CO<sub>2</sub>R: *i*) H1-01 synthesized by the hydrothermal route and exhibiting a large (0.8-1.5  $\mu$ m) prismatic-tabular morphology (Fig. 1A), *ii*) P2-02 synthesized by the precipitation route with a small (< 500 nm) sheet-like morphology (Fig. 1B) and *iii*) P2-04 synthesized by means of the precipitation route with large (0.8-1.2  $\mu$ m) sheet-like morphology (Fig. 1C). Electrocatalytic tests, performed in a dedicated flow cell set-up, confirmed that the products selectivity strongly depended on both morphology and dimensions of the CuO catalysts.



In particular, at low applied current density (50-100 mA cm<sup>-2</sup>), H1-01 favors the CO<sub>2</sub>-to-CO conversion, whereas at high current density this system becomes more unstable and less selective. Differently, at low current density, both P2-02 and P2-04 systems favor the  $CO_2$ -to- $C_2H_4$  conversion, whereas at high current density, the selectivity toward the detrimental hydrogen evolution reaction (HER) starts becoming predominant. Only the P2-04 shows an increased  $CO_2$ -to- $CH_4$  conversion selectivity.

High resolution TEM analysis and FTIR spectroscopy tests in presence of probe molecules are ongoing to clarify the role played by the morphology in term of catalytic selectivity.

The performances attained with the following three main  $Cu_2O$ -based samples in the e-CO<sub>2</sub>R is currently ongoing: *i*) F1-03 composed of small quasi spherical  $Cu_2O$  NPs with the presence of large polyhedral metallic Cu nanoparticles (NPs), *ii*) F1-07 made by small quasi spherical pure  $Cu_2O$  NPs, and *iii*) F1-12 composed of large polyhedral metallic Cu NPs (for the sake of comparison).

The obtained results will provide an effective screening of the fundamental properties necessary for maximizing the catalytic performances and specific selectivity of these systems in the e-CO<sub>2</sub>R.



**Figure 1** SEM micrographs (top) and Faradaic Efficiencies attained in the  $e-CO_2R$  test (bottom) of H1-01 (A, A'), P2-02 (B, B') and P2-04 (C, C') CuO-based materials.

### References

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