# Facile and scalable synthesis of $Cu_2O$-$SnO_2$ catalyst for the photoelectrochemical $CO_2$ conversion

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Maddalena Zoli[a,b], Daniela Roldán[a], Hilmar Guzmán[a,b], Simelys Hernández[a,b], Micaela Castellino,[a] Angelica Chiodoni[b], Katarzyna Bejtka[b], Nunzio Russo[a]

[a] *CREST group, Department of applied science and technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi, 24, 10129, Turin, Italy*
[b] *Center for Sustainable Future Technologies, IIT@Polito, Istituto Italiano di Tecnologia, Via Livorno, 60, 10144, Turin, Italy*

email: maddalena.zoli@polito.it, simelys.hernandez@polito.it

# Optimization of co-precipitation method for catalyst production

## Motivation

- The natural $CO_2$ sink cannot keep up with the constant **anthropic emission**
- A renewable and green approach to **$CO_2$ recovery** is increasingly necessary
- Ongoing development of a **$CO_2$RR photo-electrocatalyst** to convert $CO_2$ into useful chemicals or fuels

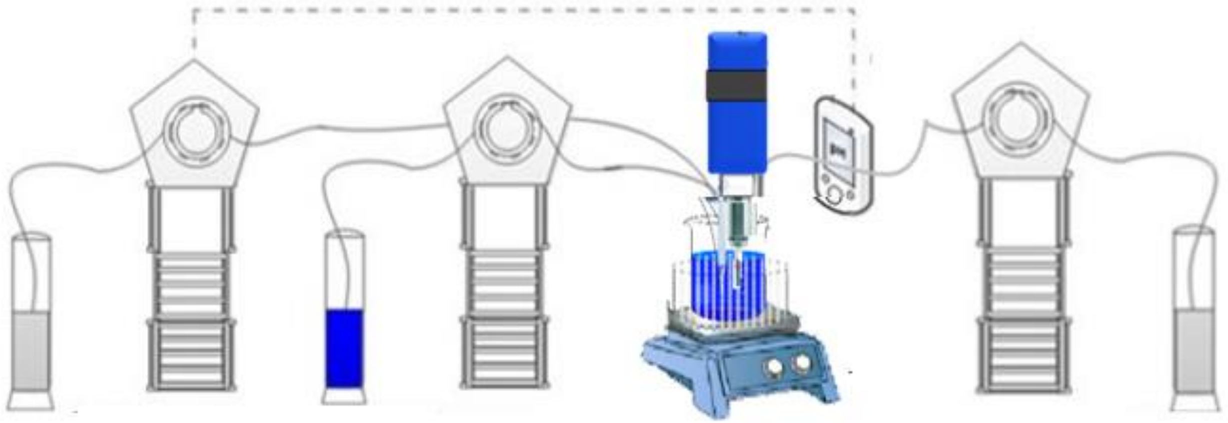
### The catalyst: $Cu_2O$-$SnO_2$

### p-n junction with:

**$Cu_2O$** ⇨ cheap, abundant, intrinsically p-type semiconductor, narrow band gap (~ 2 eV), suitable positioning of conduction and valence bands

**$SnO_2$** ⇨ n-type direct band-gap semiconductor, good electron mobility, intrinsic stability.

## Synthesis set-up



$Na_2CO_3$ Precipitant agent

$(Cu(NO_3)_2 \cdot 3H_2O + SnCl_2$ Precursor solution

Reducing Agent


- Ultra-sound assisted
- pH, T, stirring control
- Clean-up procedure optimization
- Reproducibility tests

## Catalyst Characterization

- XPS

Auger Parameter

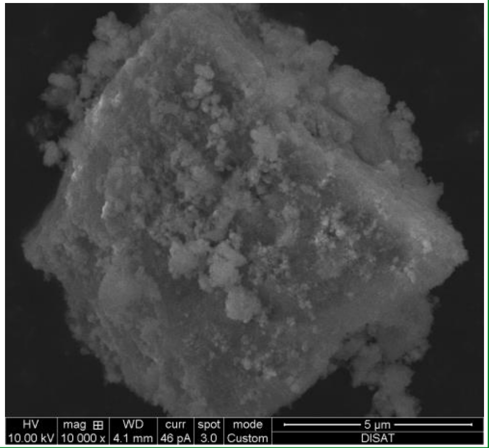
$$h\nu - CuLMM + Cu2p_{2/3} = \mathbf{1849.4\ eV}$$

| Element | Cu | Sn | O | Cl |
|---|---|---|---|---|
| Atomic % | 10.44 ± 0.86 | 11.01 ± 0.24 | 41.10 ± 2.13 | 0.85 ± 0.59 |

Resulting oxidation states abundance

Cu(II) 57 %
Cu(0)+Cu(I) 43 %

- FESEM



maddalena.zoli@polito.it

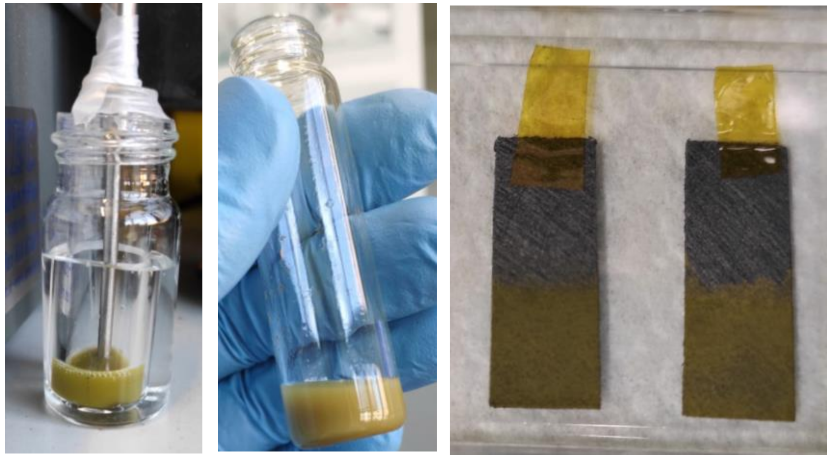
# Electrodes development

## Preparation and deposition

- **Fixed** catalyst to Nafion (binder) **ratio**
- **Ethanol** studied as the best carrier because of its low boiling temperature

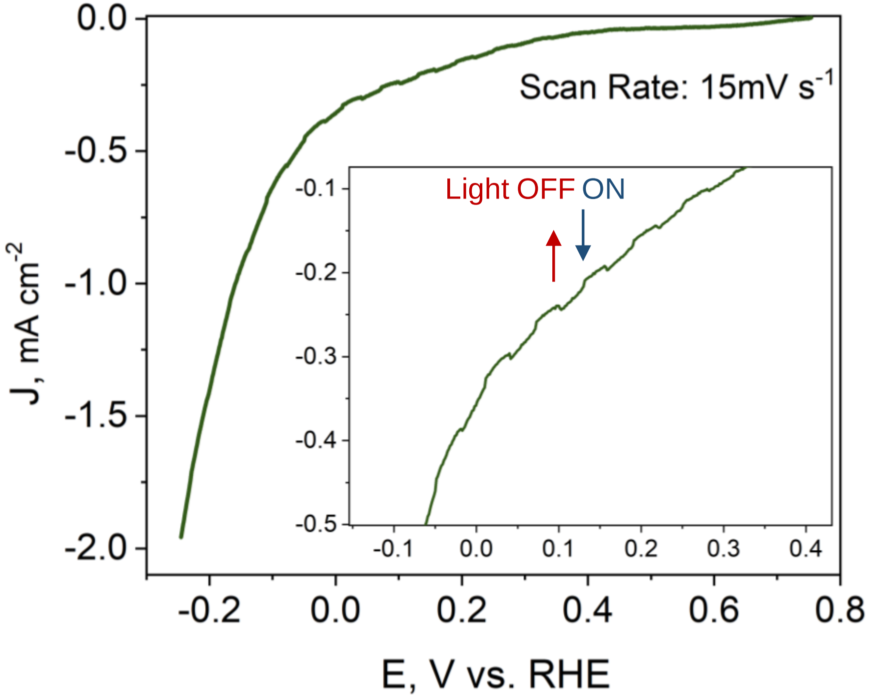
- Ultrasonic tip used to create the "**ink**"
- Deposition on porous conductive support: GDL (Gas Diffusion Layer), by **airbrushing**

## Preparation Steps



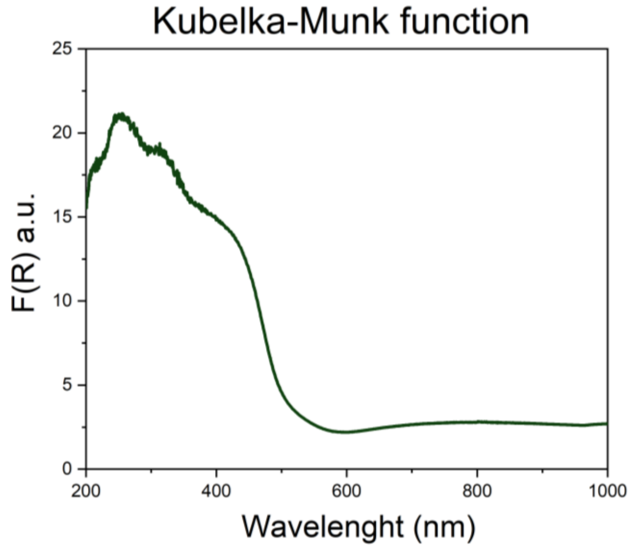
## Photoactivity evidence

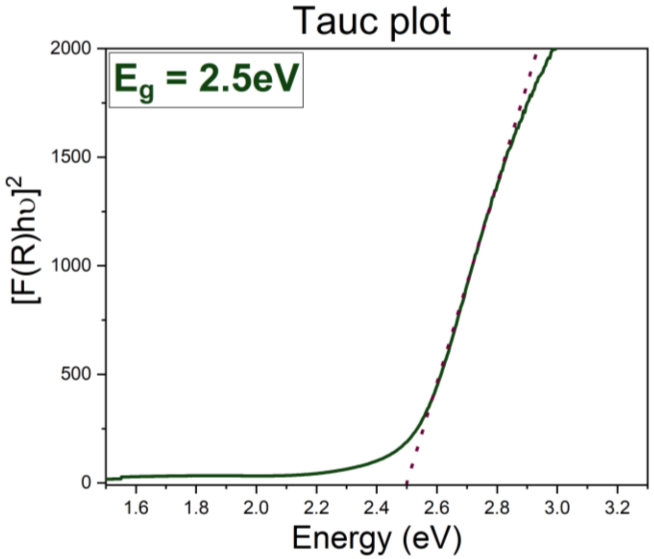
Linear Sweep Voltammetry (LSV)
(the inset illustrates a zoomed frame of the curve)




- The current pattern follows the light switching on/off.

## Optical Properties (UV-Vis)

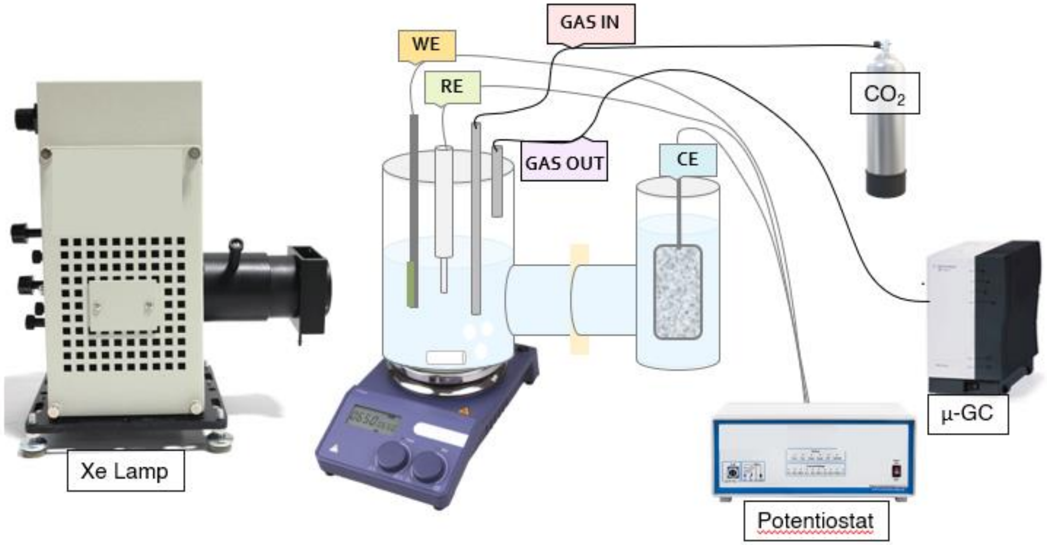



maddalena.zoli@polito.it

# Photo-electrocatalytic $CO_2$ reduction test

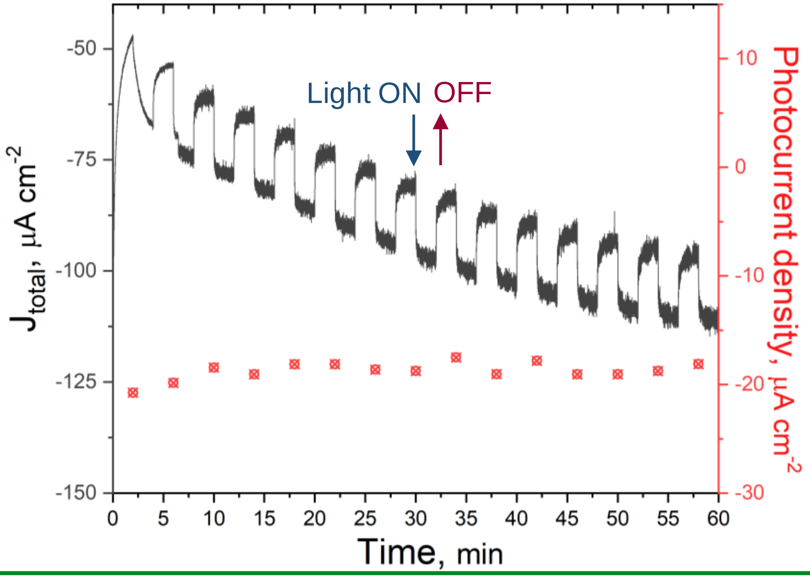
## Photo-electrocatalytic $CO_2$ reduction set-up



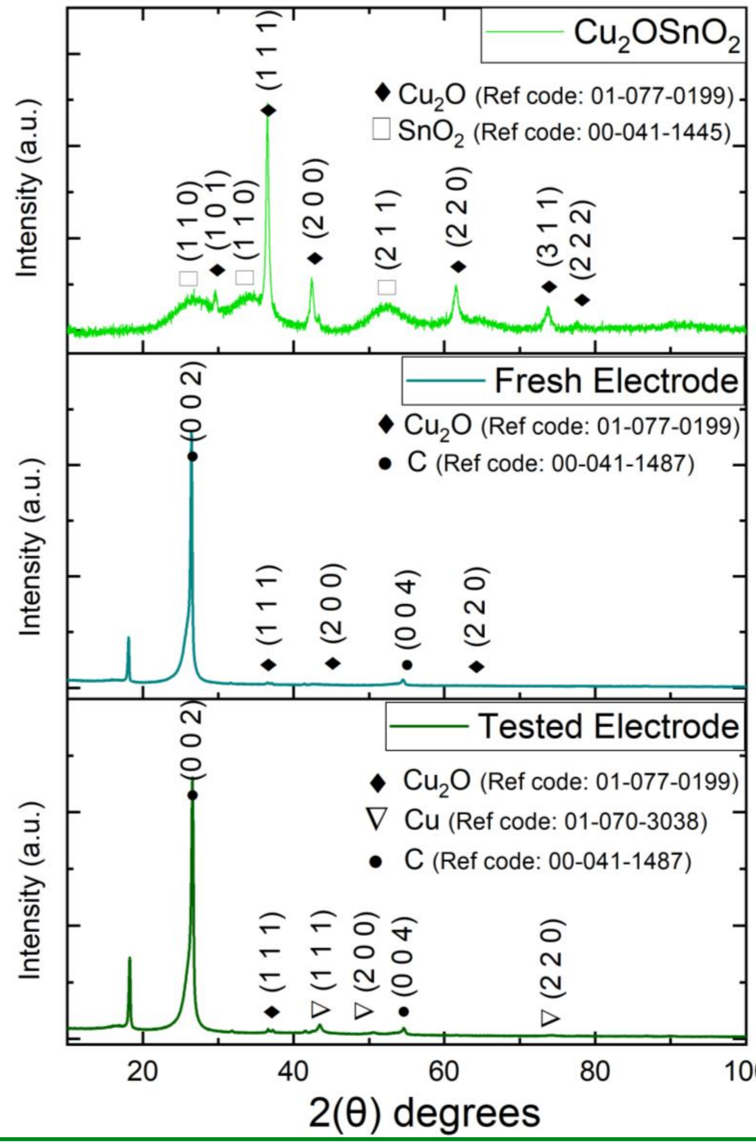

## Photocurrent contribution

Photoelectrochemical performance (J vs. time) of $Cu_2OSnO_2$ photocathode towards $CO_2$ reduction driven under simulated solar irradiation in a $CO_2$-saturated 0.1M $KHCO_3$ solution at 0.50V vs. RHE

- Grey line ⟹ current evolution
- Red points ⟹ photocurrent contribution, average value **-18.75 μA cm$^{-2}$**




## XRD Spectra

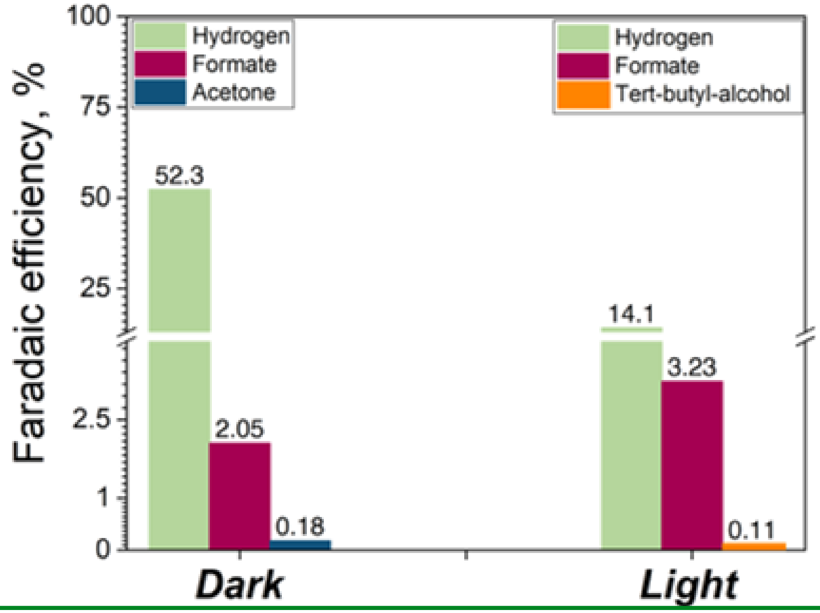


# PEC $CO_2$ reduction products and future developments

## Faradaic Efficiencies

Photoelectrochemical $CO_2$ reduction gas and liquid products analysis

- **Products composition changes** depending on the cell lighting
- The test carried out in **light** (right) produces **less $H_2$** by a factor 3.7 and **more C-compounds** quantity (3.25 vs. 2.25 %).




## Future prospectives

- Improve the **protection of the Cu(I)** species, in order to maintain the catalyst photoactivity.
- Enhance the **light harvesting efficiency** and produce internal photovoltage for the $CO_2$RR, to expand the range of products and their Faradaic efficiencies

In the SunCoChem Project framework:

- Design of smart **organometallic chromophores** to be anchored onto the catalyst surface, playing the **double role** of $CO_2$ reduction co-catalyst and visible light absorber.

## Conclusions

- A simple, scalable and reproducible co-precipitation method for the synthesis of a Cu-Sn-based photoelectrocatalyst was developed.
- **$Cu_2O$ species were detected** in both the powder and onto the prepared electrode.
- A constant **photocurrent contribution** (~18 μA $cm^{-2}$) was achieved.
- Products composition varies depending on the light conditions.
- **$H_2$** evolution reaction is **suppressed** by the $Cu_2O$-$SnO_2$ photo-electrocatalyst.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maddalena.zoli@polito.it