Facile and scalable synthesis of Cu2O-SnO2 catalyst for the photoelectrochemical CO2 conversion

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

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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_2RR photo-electrocatalyst** to convert CO_2 into useful chemicals or fuels

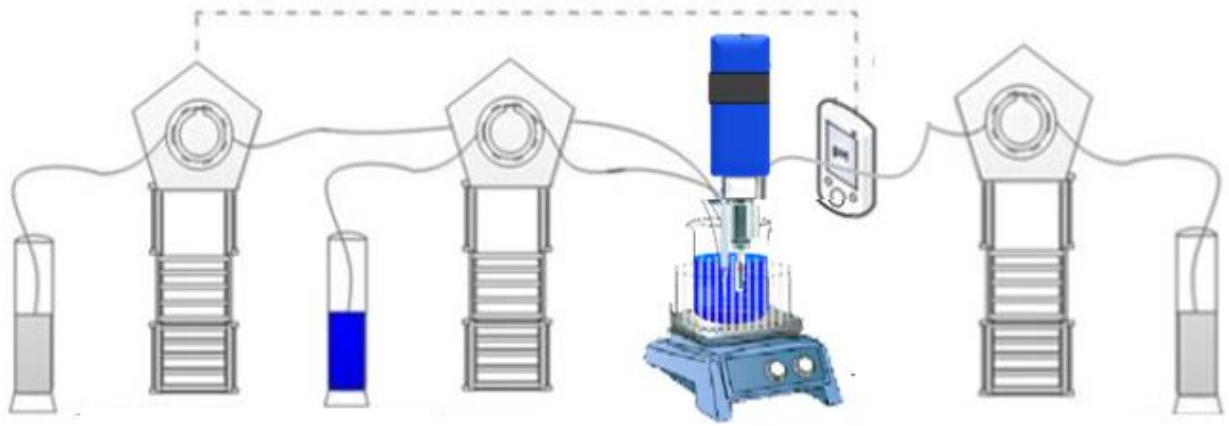
The catalyst: Cu_2O-SnO_2

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

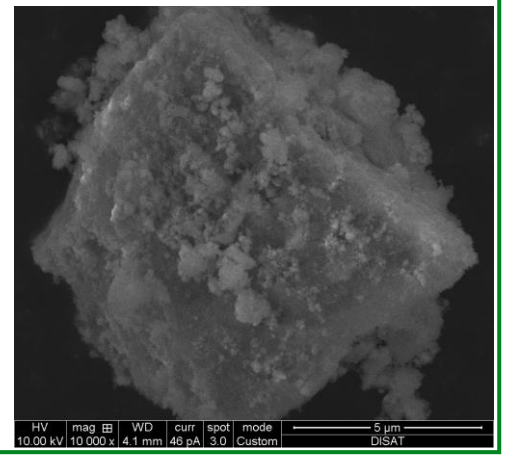
$$hv - CuLMM + Cu2p_{2/3} = \mathbf{1849.4\ eV}$$

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



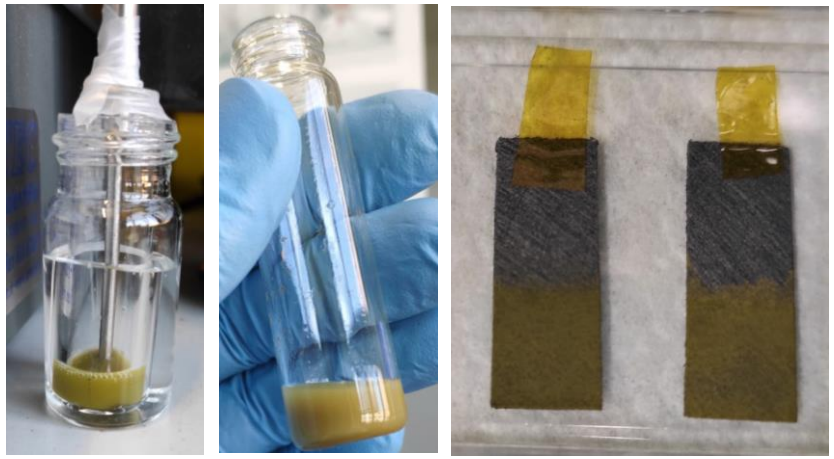
Electrodes development

Preparation and deposition

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

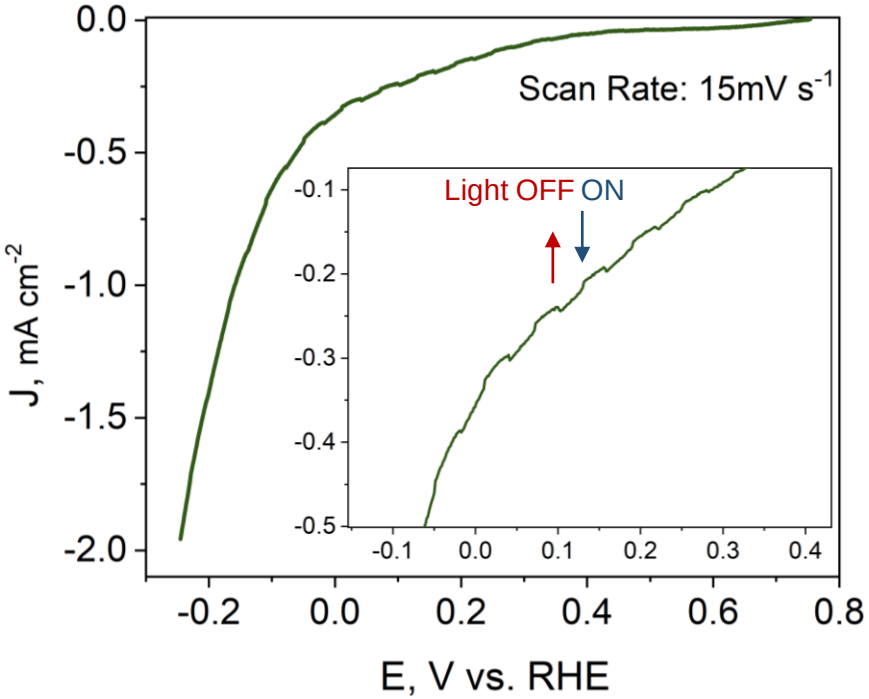
- Ultrasonic tip used to create the "**ink**"
- Deposition on porous conductive support: GDL (Gas Diffusion Layer), by **airbrushing**

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)

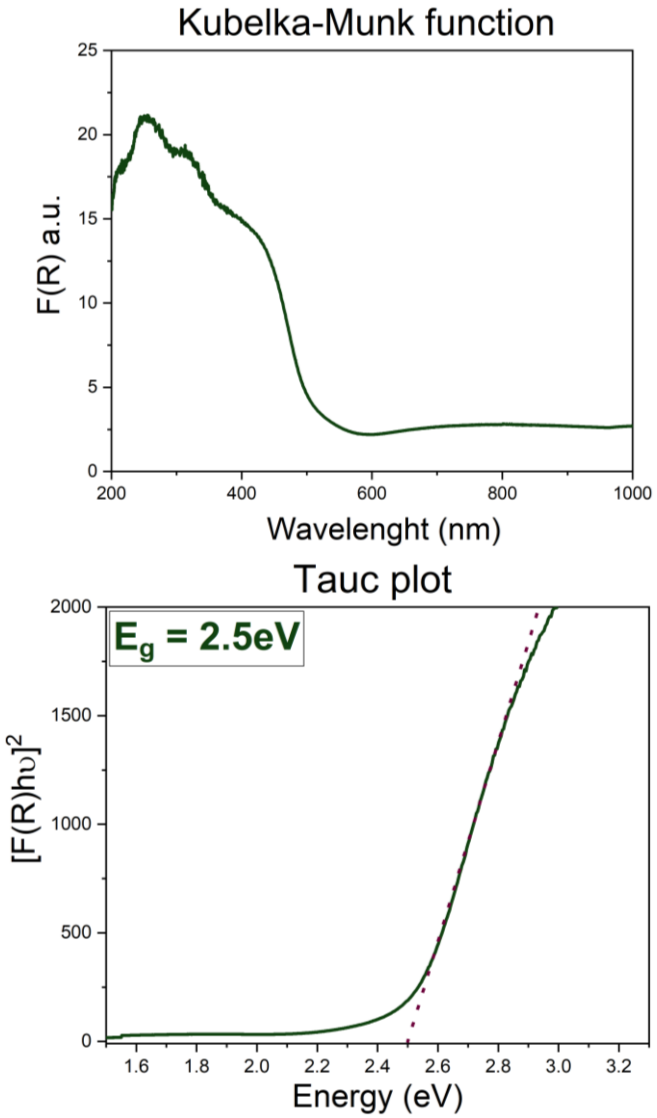


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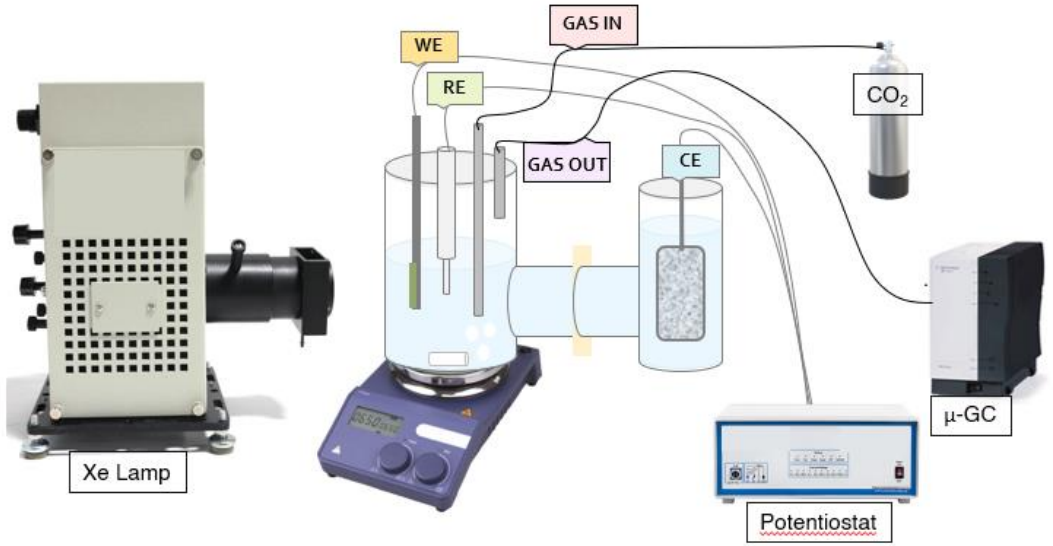
Photo-electrocatalytic CO_2 reduction test

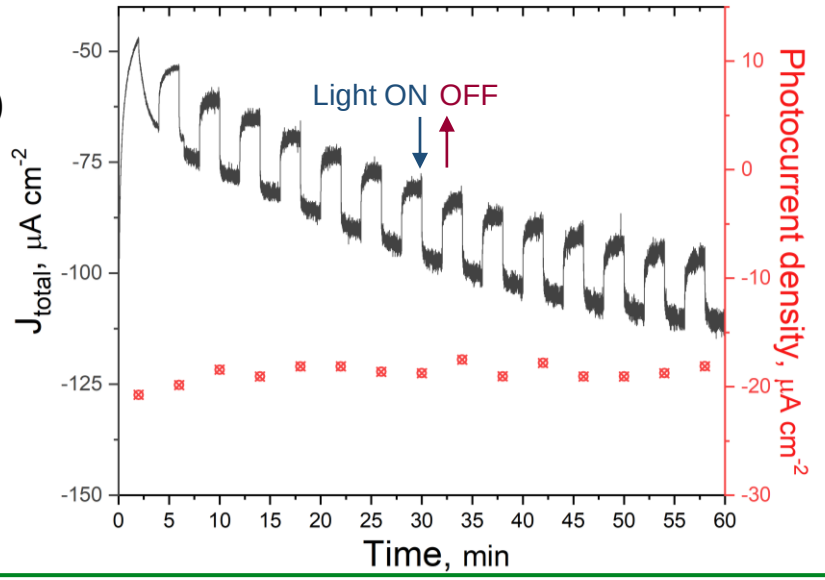
Photo-electrocatalytic CO_2 reduction set-up



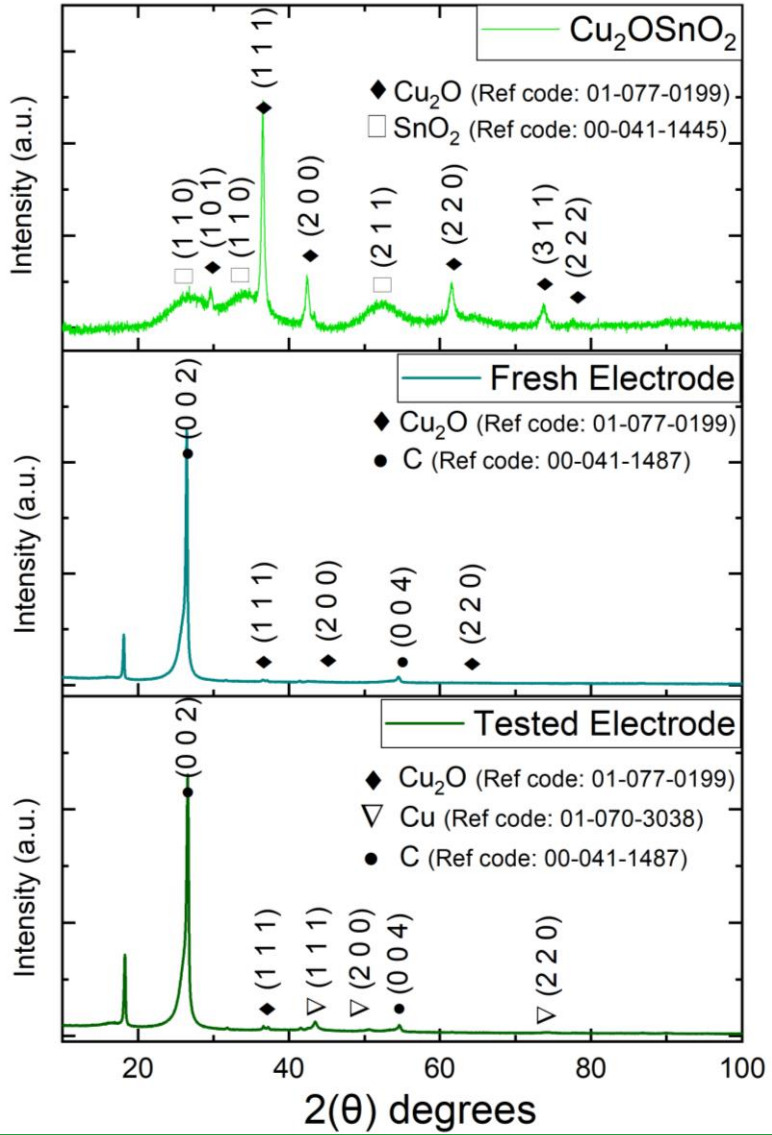
Photocurrent contribution

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

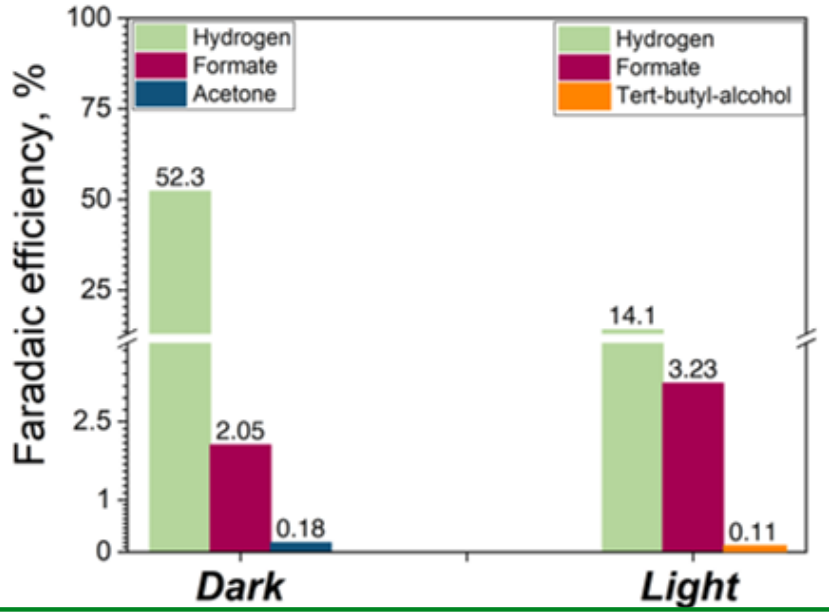


PEC CO_2 reduction products and future developments

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 %).



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.

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_2RR, 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.

SunCO2Chem

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