



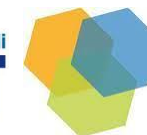
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SPRING MEETING & EXHIBIT



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CREST
Catalytic Reaction
Engineering for
Sustainable Technologies

Facile and scalable synthesis of $\text{Cu}_2\text{O-SnO}_2$ catalyst for the photoelectrochemical CO_2 conversion

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Motivation

- The natural CO₂ sink cannot keep up with the constant **anthropic emission**
- A renewable and green approach to **CO₂ recovery** is increasingly necessary
- Ongoing development of a **CO₂RR photo-electrocatalyst** to convert CO₂ into useful chemicals or fuels

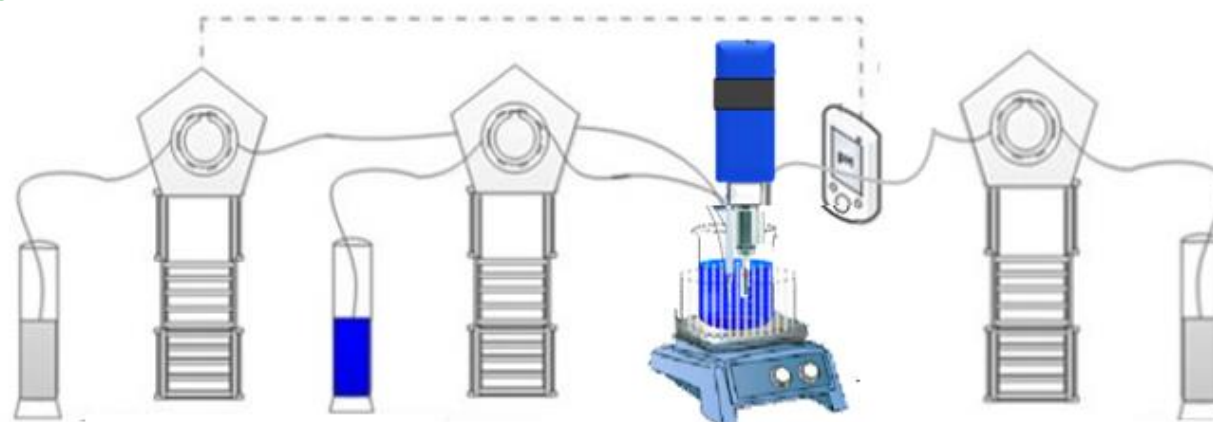
The catalyst: Cu₂O-SnO₂

p-n junction with:

Cu₂O \longrightarrow cheap, abundant, intrinsically p-type semiconductor, narrow band gap (~ 2 eV), suitable positioning of conduction and valence bands

SnO₂ \longrightarrow n-type direct band-gap semiconductor, good electron mobility, intrinsic stability.

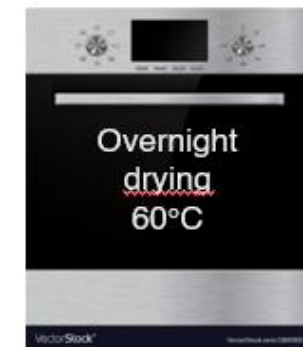
Synthesis set-up



Na₂CO₃
Precipitant agent

(Cu(NO₃)₂ · 3H₂O + SnCl₂)
Precursor solution

Reducing Agent



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

Catalyst Characterization

- XPS

Auger Parameter

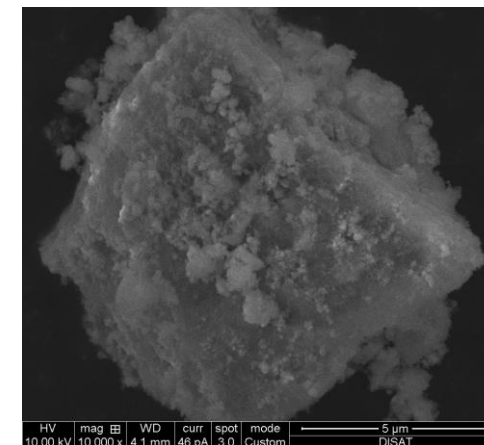
$$h\nu - CuLMM + Cu2p_{2/3} = 1849.4 \text{ eV}$$

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 %

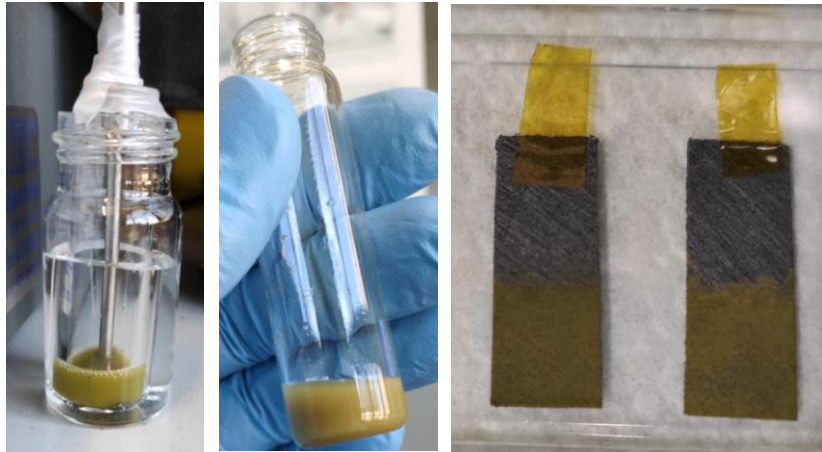
- FESEM



Preparation and deposition

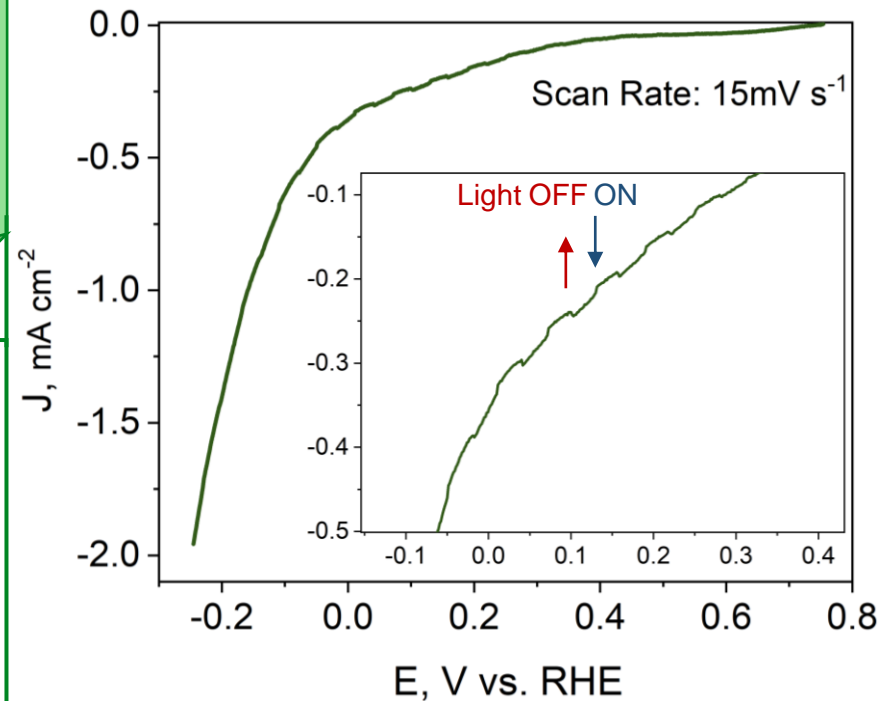
- **Fixed** catalyst to Nafion (binder) **ratio**
- **Ethanol** studied as the best carrier because of its low boiling temperature
- Ultrasonic tip used to create the “**ink**”
- Deposition on porous conductive support: GDL (Gas Diffusion Layer), by **airbrushing**

Preparation Steps



Photoactivity evidence

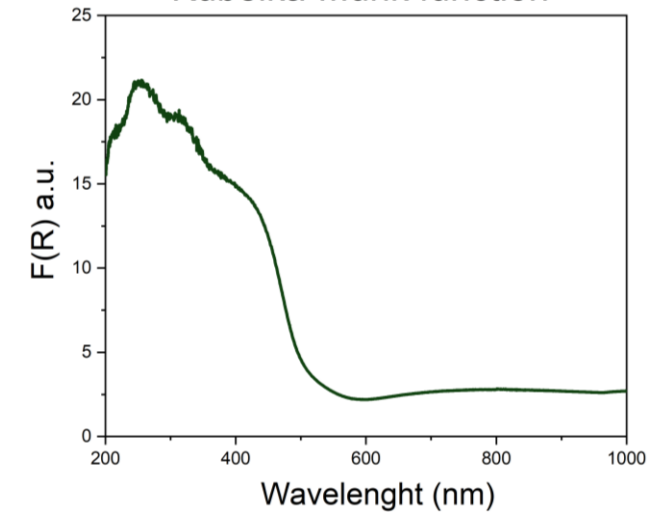
Linear Sweep Voltammetry (LSV)
(the inset illustrates a zoomed frame of the curve)



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

Optical Properties (UV-Vis)

Kubelka-Munk function



Tauc plot

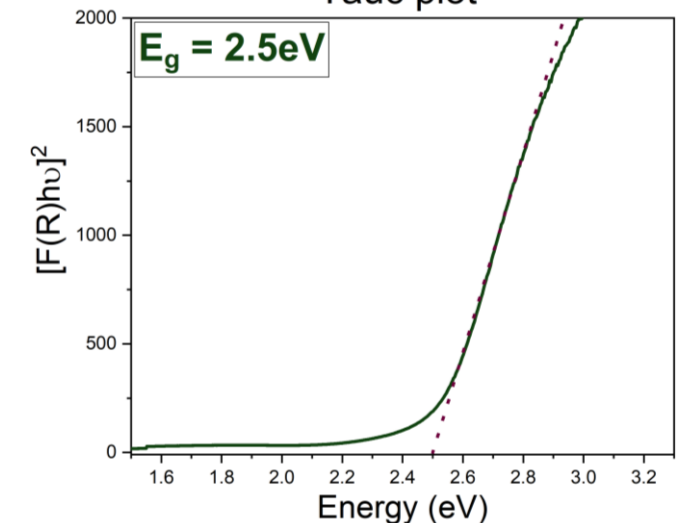
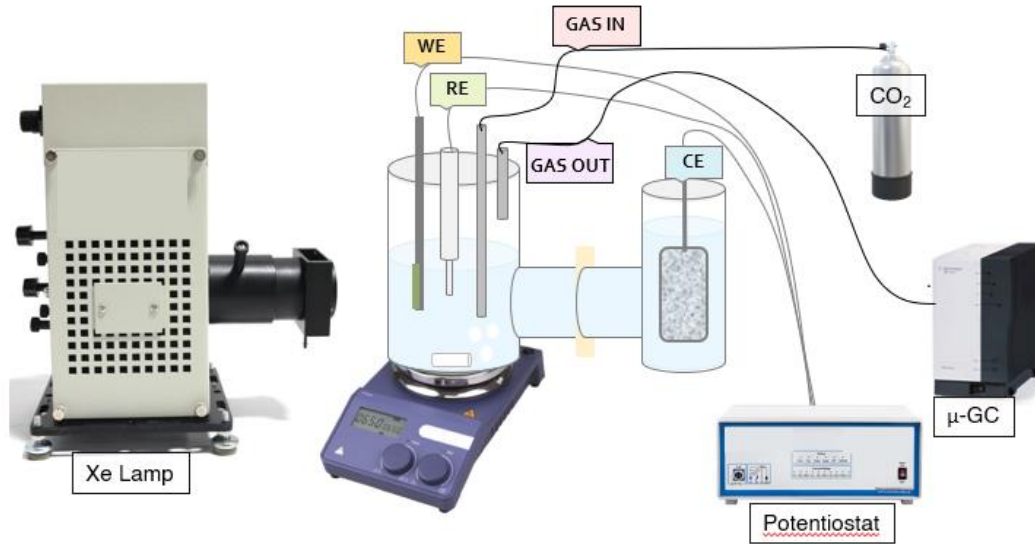
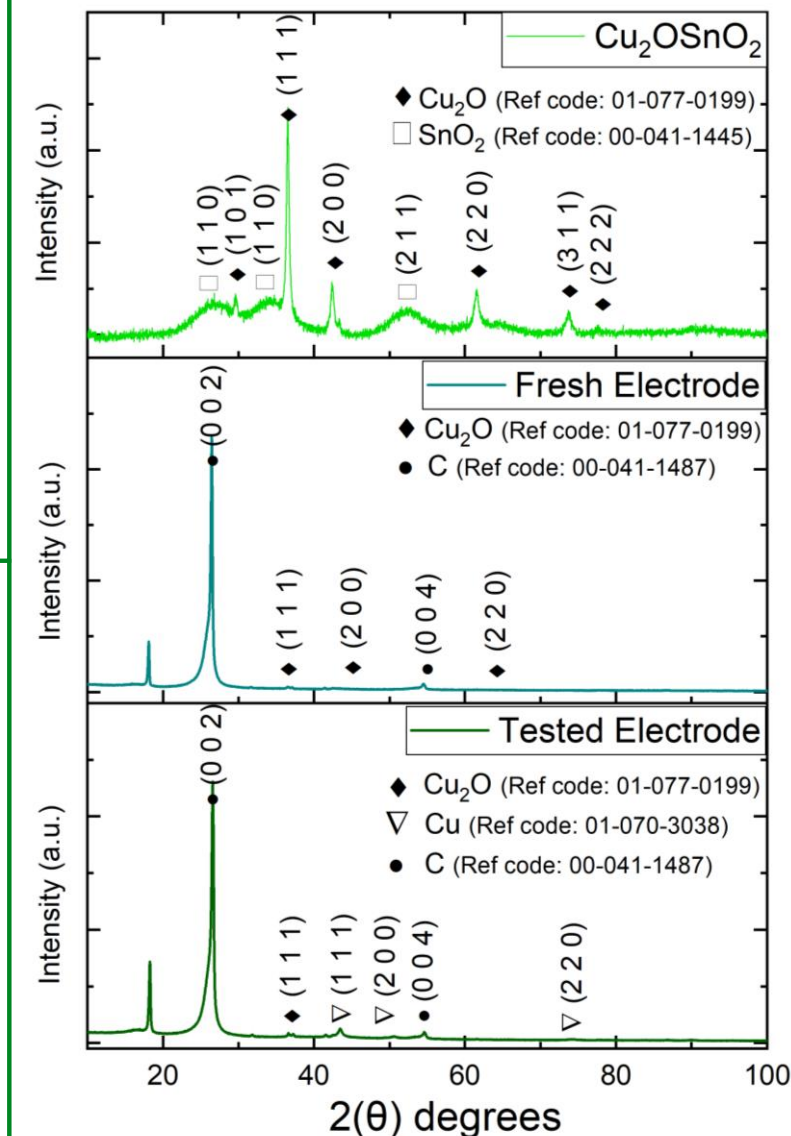


Photo-electrocatalytic CO₂ reduction set-up



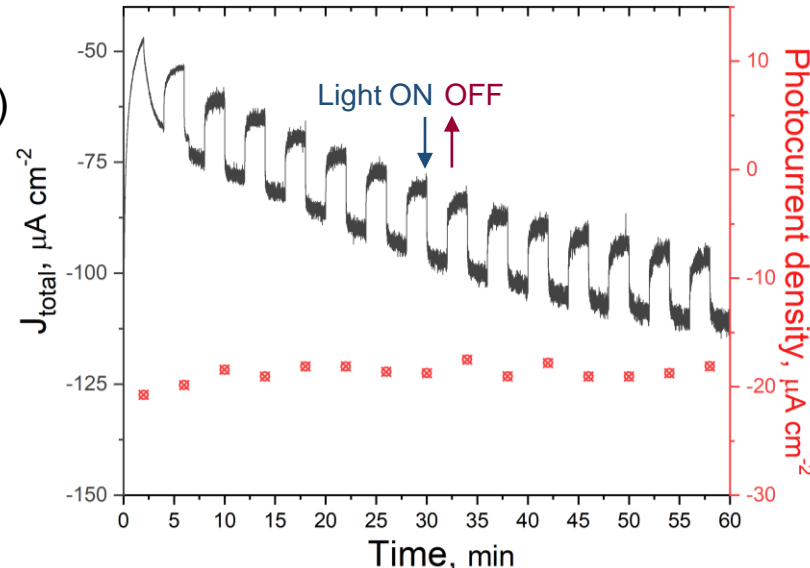
XRD Spectra



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

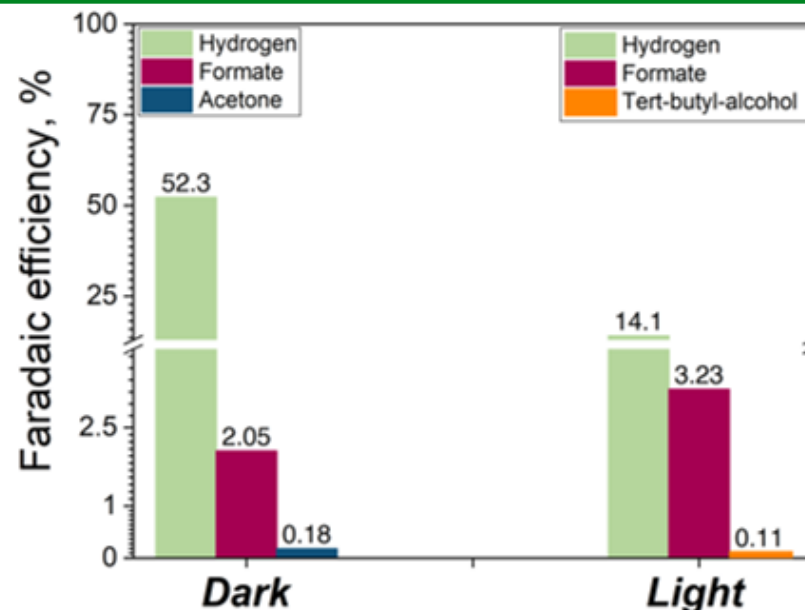
- Grey line current evolution
- Red points photocurrent contribution, average value $-18.75 \mu\text{A cm}^{-2}$



Faradaic Efficiencies

Photoelectrochemical CO₂ reduction gas and liquid products analysis

- **Products composition changes** depending on the cell lighting
- The test carried out in **light** (right) produces **less H₂** by a factor 3.7 and **more C-compounds** quantity (3.25 vs. 2.25 %).



Future perspectives

- 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 CO₂RR, 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 CO₂ 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.
- **Cu₂O 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.
- H₂ evolution reaction is **suppressed** by the Cu₂O-SnO₂ photo-electrocatalyst.



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