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

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Facile and scalable synthesis of Cu$_2$O-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$_2$RR *photo-electrocatalyst* to convert CO$_2$ into useful chemicals or fuels

The catalyst: Cu$_2$O-SnO$_2$

*p-n* junction with:

Cu$_2$O 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

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

Catalyst Characterization

- **XPS**

  Auger Parameter

  $h\nu - Cu LMM$

  \( Cu_{2p_2/3} \)

  \( = 1849.4 \, eV \)

  

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Sn</th>
<th>O</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic %</td>
<td>10.44 ± 0.86</td>
<td>11.01 ± 0.24</td>
<td>41.10 ± 2.13</td>
<td>0.85 ± 0.59</td>
</tr>
</tbody>
</table>

  Resulting oxidation states abundance

  Cu(II) 57 %

  Cu(0)+Cu(I) 43 %

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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**

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**
- **E_g = 2.5 eV**

Preparation Steps

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Photo-electrocatalytic CO₂ reduction test

Photo-electrocatalytic CO₂ reduction set-up

XRD Spectra

Photocurrent contribution

Photoelectrochemical performance (J vs. time) of Cu₂OSnO₂ photocathode towards CO₂ reduction driven under simulated solar irradiation in a CO₂-saturated 0.1M KHCO₃ solution at 0.50V vs. RHE

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

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PEC CO₂ reduction products and future developments

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.

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.

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.

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