

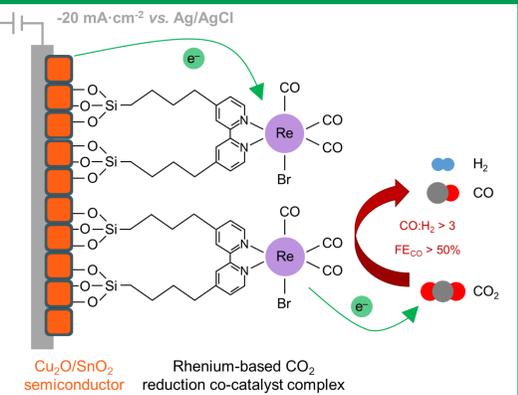
Scalable Synthesis of Stable Core-Shell Cu₂O/SnO₂ Nanoparticles For The Electrochemical CO₂ Conversion

ABSTRACT

The concept of carbon dioxide (CO₂) conversion into useful chemicals through electrochemical reduction processes constitutes a remarkable strategy for enabling negative carbon emission into the atmosphere.[1] Different electrocatalytic methods based on Cu₂O nanoparticles for cathode applications have raised increasing interest in recent years, and various small-scale studies are present in the literature. However, stability of Cu₂O catalysts for CO₂ reduction remains a challenge, and very few reports are available on it.[2] Recently, it was reported that modifying Cu₂O with a controlled amount of SnO₂ can significantly enhance the stability and the Faradaic efficiency (FE) of copper-based electrocatalysts towards CO.[3]

Herein, we report a scalable and low-cost process for producing core-shell Cu₂O/SnO₂ nanoparticles functionalized with a silane group. A simple and versatile methodology based on wet precipitation of a SnO₂ shell onto Cu₂O core nanoparticles followed by silanization has been optimized at pilot scale. Finally, a rhenium-based CO₂ reduction co-catalyst complex has been assembled by electropolymerization giving the metal complex-semiconductor hybrid electro-cathode. The carbon paper-supported electro-cathode was characterized at 10 cm² scale, demonstrating a steady-state production of syngas (>50% FE CO) at -20 mA·cm⁻² for 3 hours, and achieving a CO:H₂ ratio higher than 3.

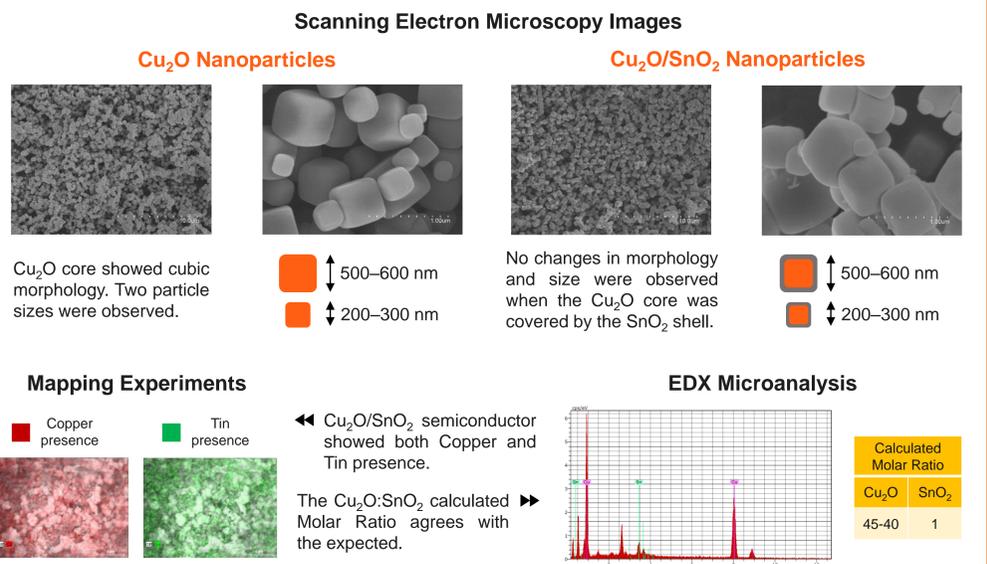
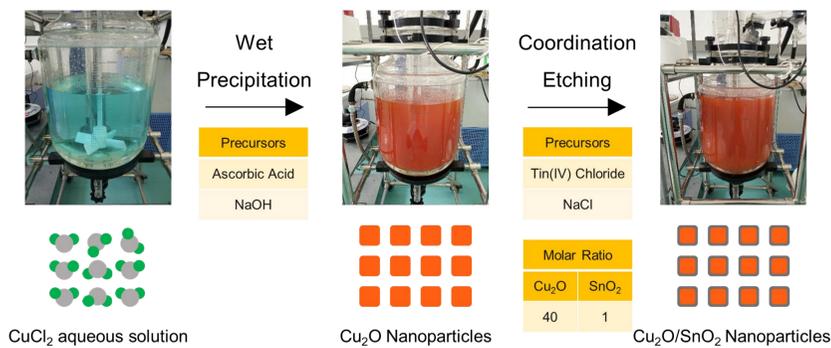
Keywords: CO₂ reduction, Cu₂O/SnO₂ semiconductor, pilot scale, silanization, metal complex-semiconductor hybrid electro-cathode.



ELECTRO-CATHODE PREPARATION PROCESS AND CHARACTERIZATION

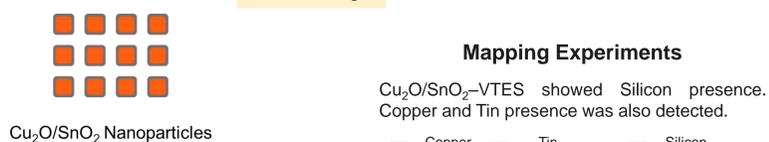
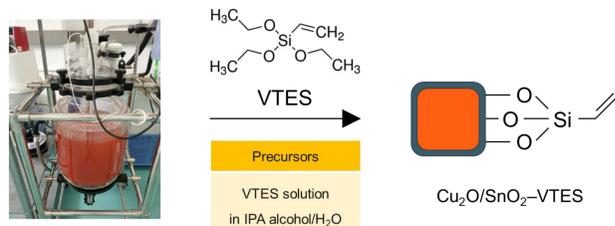
1 Cu₂O/SnO₂ Semiconductor Preparation Process

FIRST STEP in the electro-cathode preparation process was the Cu₂O/SnO₂ semiconductor synthesis. The methodology was easy-to-scale and low-cost and consisted in a two-step procedure involving (1) wet precipitation[4] followed by (2) coordination etching[5].

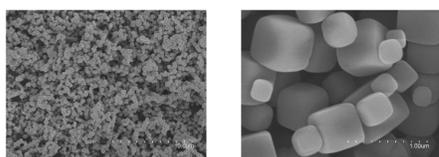


2 Cu₂O/SnO₂ Functionalization with VTES

Functionalization with VTES (VinylTriEthoxySilane) was the SECOND STEP during the electro-cathode preparation process. The methodology was also easy-to-scale and consisted in a one-step reaction where the previously obtained Cu₂O/SnO₂ semiconductor was suspended in a VTES solution in IPA alcohol/H₂O.



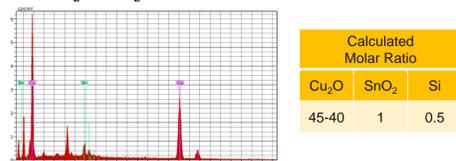
Scanning Electron Microscopy Images



No remarkable changes in both morphology and size were observed. Functionalized Cu₂O/SnO₂-VTES showed cubic morphology with sizes in the range 300–700 nm.

EDX Microanalysis

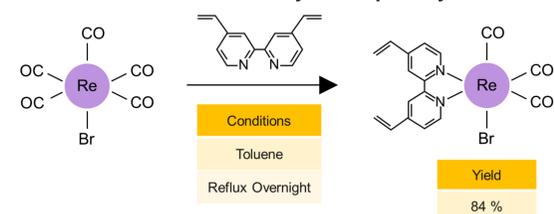
Functionalization with VTES did not modify Cu₂O:SnO₂ calculated Molar Ratio.



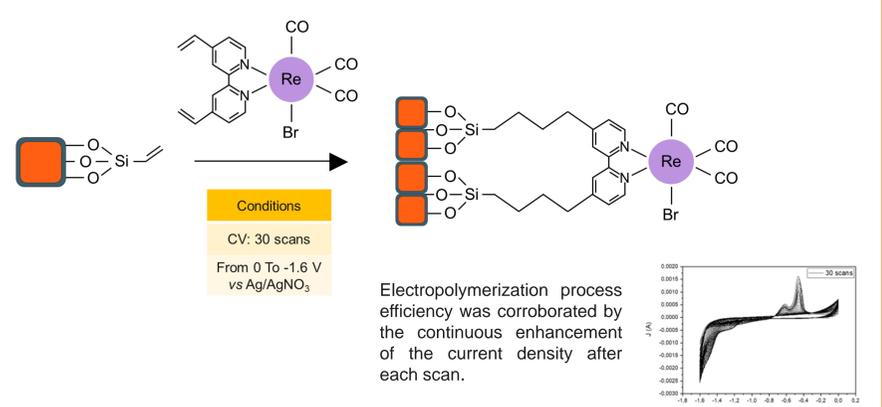
3 Electropolymerization with Rhenium-based co-catalyst

Electropolymerization reaction between the Cu₂O/SnO₂-VTES semiconductor and the rhenium-based CO₂ reduction co-catalyst complex was the FINAL STEP concerning the electro-cathode preparation process. Electropolymerization process implied the vinyl groups reduction to form radical couplings and the subsequent Carbon-Carbon bond formation.

Rhenium-based co-catalyst complex Synthesis



Electropolymerization with Rhenium-based co-catalyst complex



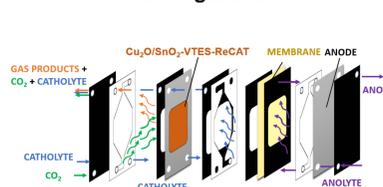
CONCLUSIONS

Low-cost and easy-to-scale methodology for producing p-type core-shell Cu₂O/SnO₂ semiconductor was here reported. The characterization by Scanning Electron Microscopy demonstrated the methodology showed good reproducibility. Functionalization with VTES was successful and no changes in Cu₂O/SnO₂ semiconductor physical and chemical properties were noticed when VTES was incorporated. Electropolymerization with the Rhenium-based co-catalyst complex lead to the final metal complex-semiconductor hybrid electro-cathode. The carbon paper-supported electro-cathode produced CO for 3 hours at the target current density and remained stable during the electrochemical characterization.

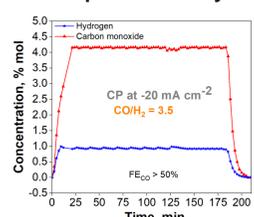
ELECTRO-CATHODE PERFORMANCE

A long-term test (3 hours) at 10 cm² scale with a Cu₂O/SnO₂-ReCAT electrode (1 mg·cm⁻²) tested in an aqueous electrolyte showed good stability towards CO production, with a final CO/H₂ ratio of 3.5 at the target current density (-20 mA·cm⁻²).

Electrochemical Configuration



Products Trend during Chronopotentiometry Test



REFERENCES

- [1] H.-R. Jhong, S. Ma, and P.J.A. Kenis. *Curr. Opin. Chem. Eng.* **2013**, 2, 191.
- [2] R. Kas, R. Kortlever, A.r Milbrat, M.T.M. Koper, G. Mul, and J. Baltrusaitis. *Phys. Chem. Chem. Phys.* **2014**, 16, 12194.
- [3] S.-N. Zhang, M. Li, B. Hua, N. Duan, S. Ding, S. Bergens, K. Shankar, and J.-L. Luo. *ChemCatChem.* **2019**, 11, 4147.
- [4] D.-F. Zhang, H. Zhang, L. Guo, K. Zheng, X.-D. Han, and Z. Zhang. *J. Mater. Chem.* **2009**, 19, 5220.
- [5] Z. Wuang, D. Luan, F.Y. Boey, and X.W. Lou. *J. Am. Chem. Soc.* **2011**, 133, 4738.

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