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CONCLUSION

- Novel, fast and cheap chemical method for sulfidation of metallic Cu at room temperature.
- The reaction mechanism on which the synthesis method is based is still unknown.
- The main sulfide phase (70-90 wt.%) is digenite and the secondary one is roxbyite. Both have identical stoichiometry i.e. Cu_{1.8}S.
- The CO₂ER activity measurements show that this material can convert CO₂ into HCOOH with ~65% Faradaic Efficiency at -0.7 vs RHE, that is 3.6-fold higher when compared to pristine Cu-mesh.
- The sulfidized Cu-mesh maintain 15-fold higher surface roughness than the pristine Cu-mesh under CO₂-electrolysis conditions.
- The SEM shows that flower-like structures are formed from the Cu_{1.8}S coating during the CO₂-electrolysis process.
- Ex situ XPS shows that the Cu/S ratio is relatively decreased after the CO₂-electrolysis process, even though the S 2p signals are rather noisy.
- A better understanding of the role and nature of the residual sulfur on the Cu-oxidation state and thus HCOOH selectivity could be achieved by implementing in situ methods (XPS and Raman) and HR-TEM and EELS.

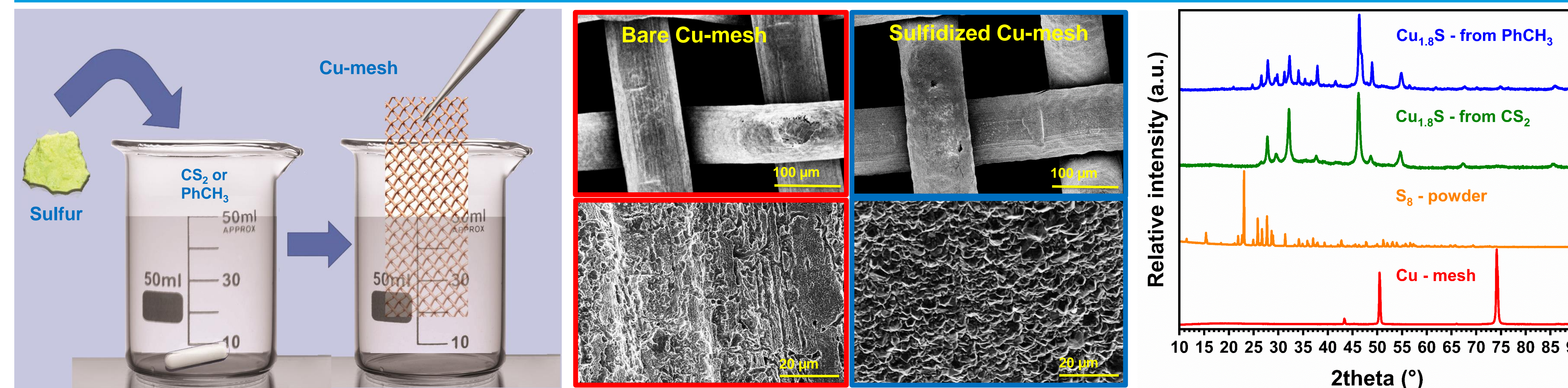
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The research group EE-NECC is supported by the Helmholtz Association *Initiative and Networking Fund* and by Helmholtz-Zentrum Berlin für Materialien und Energie

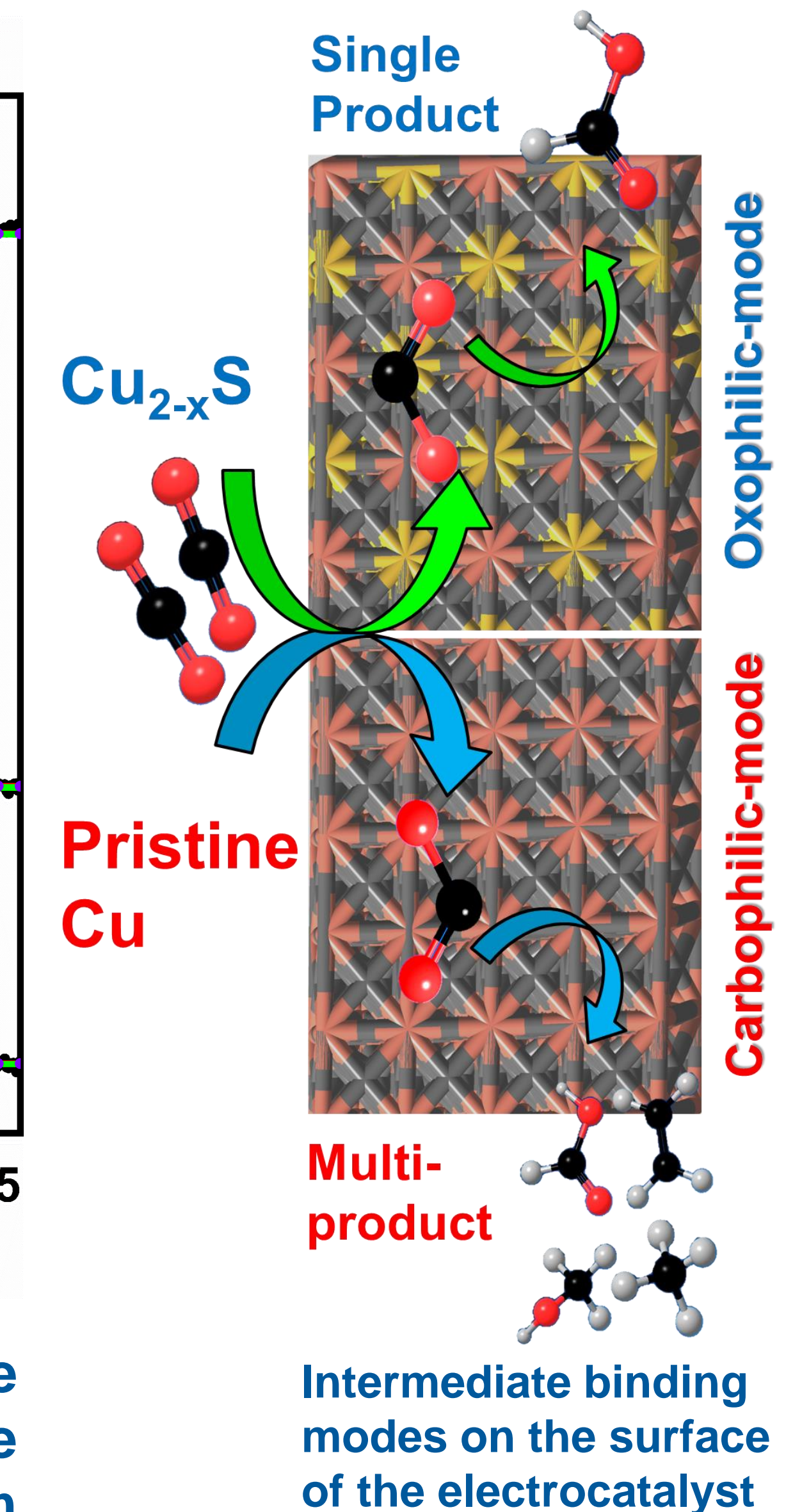
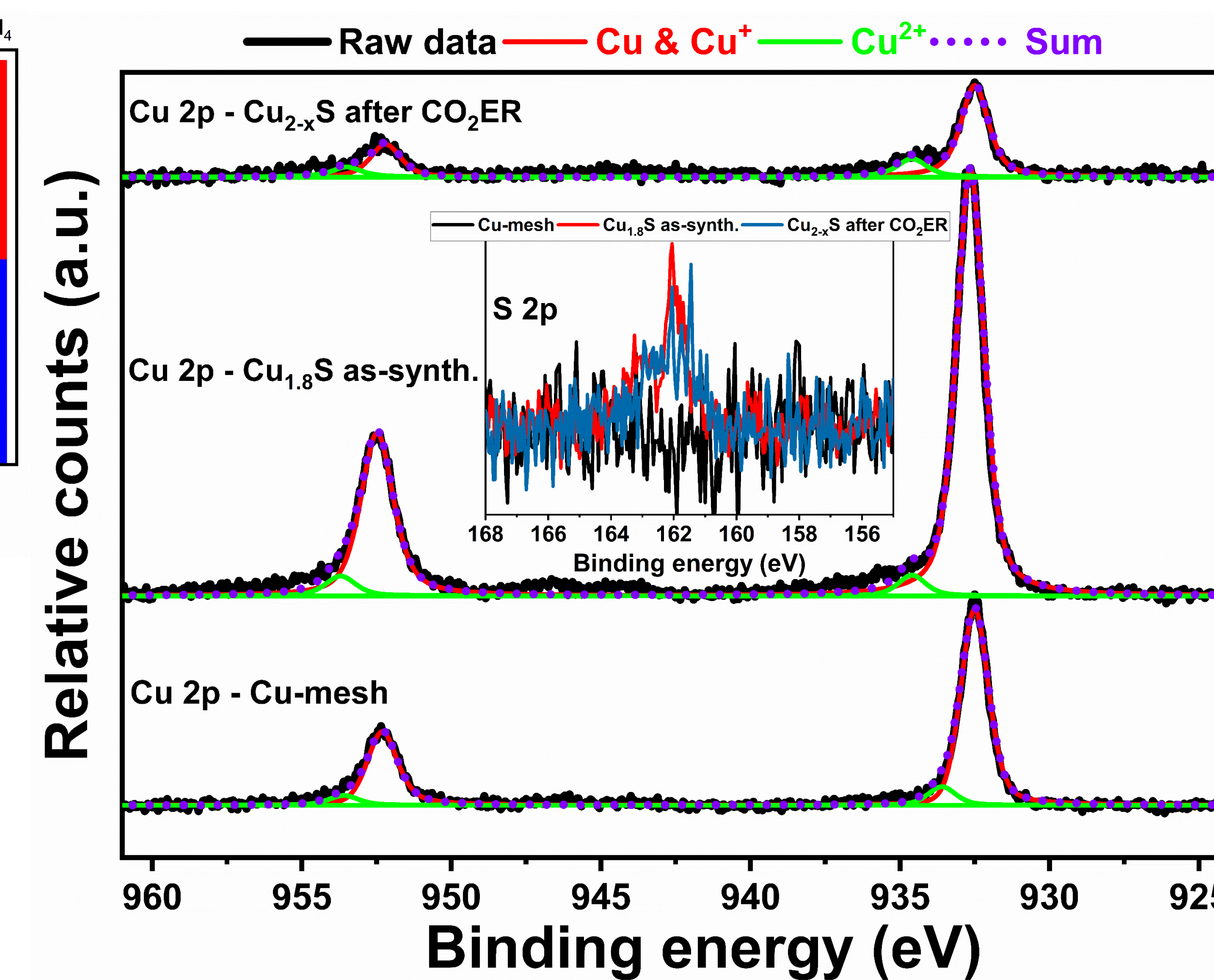
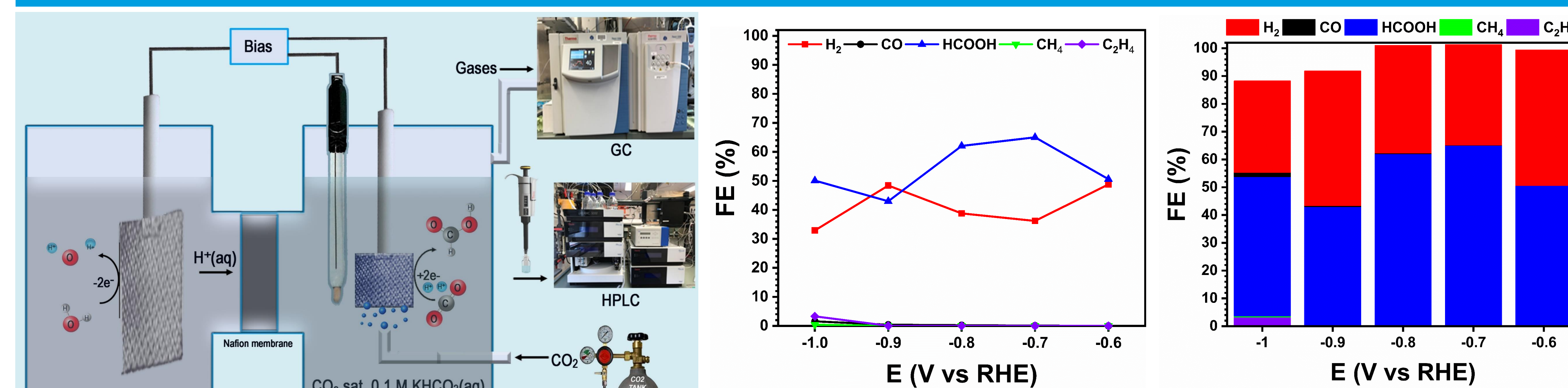
Introduction

Formic acid (HCOOH) is valuable feedstock chemical used in broad industrial fields as well as in fuel cells.^[1] The production of HCOOH via renewable energy driven electrochemical reduction of CO₂ (CO₂ER) is a promising strategy which combines renewable chemical synthesis, CO₂ emissions mitigation, and energy storage. Various materials have been investigated as promising electrocatalyst materials for selective and efficient CO₂ conversion into formate (e.g., Sn, Pb, In and Cu_xS).^[2-6] Among them, copper sulfide based electrocatalysts (Cu_{2-x}S) are promising candidates due to their activity, non-toxicity, and chemical abundance.^[4-6] Moreover, the properties of Cu_{2-x}S can be tuned by adjusting their stoichiometry, morphology and structure.^[6] Synthesis of Cu_xS with defined shape, size distribution, controlled stoichiometry, and defined crystal structure via a simple, low cost, and scalable processes is rather challenging.^[6] We propose a simple, novel and inexpensive route for synthesis of cuprous sulfides via a direct reaction between elemental copper and sulfur dissolved in CS₂ and PhCH₃ at room temperature. The as-synthesized materials were characterized using variety of techniques including SEM, XRD and XPS. The electrochemical measurements showed that HCOOH is the only CO₂ER product (at ≤ -0.8 V vs RHE in CO₂ sat. 0.1 M KHCO₃). Further study is required to provide insight into the nature of the active site and the role of sulfur, and the subsequent mechanistic implications with reference to the conventionally described shift from carbophilic to oxophilic binding which characterizes the HCOOH pathway.

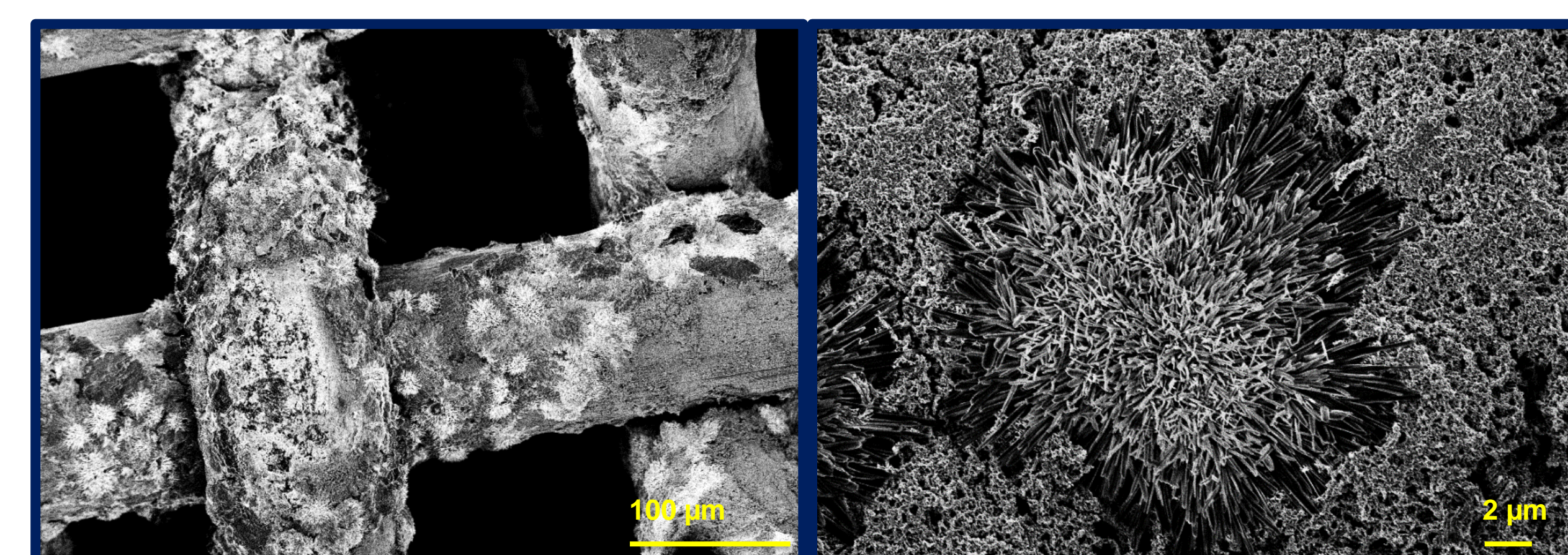
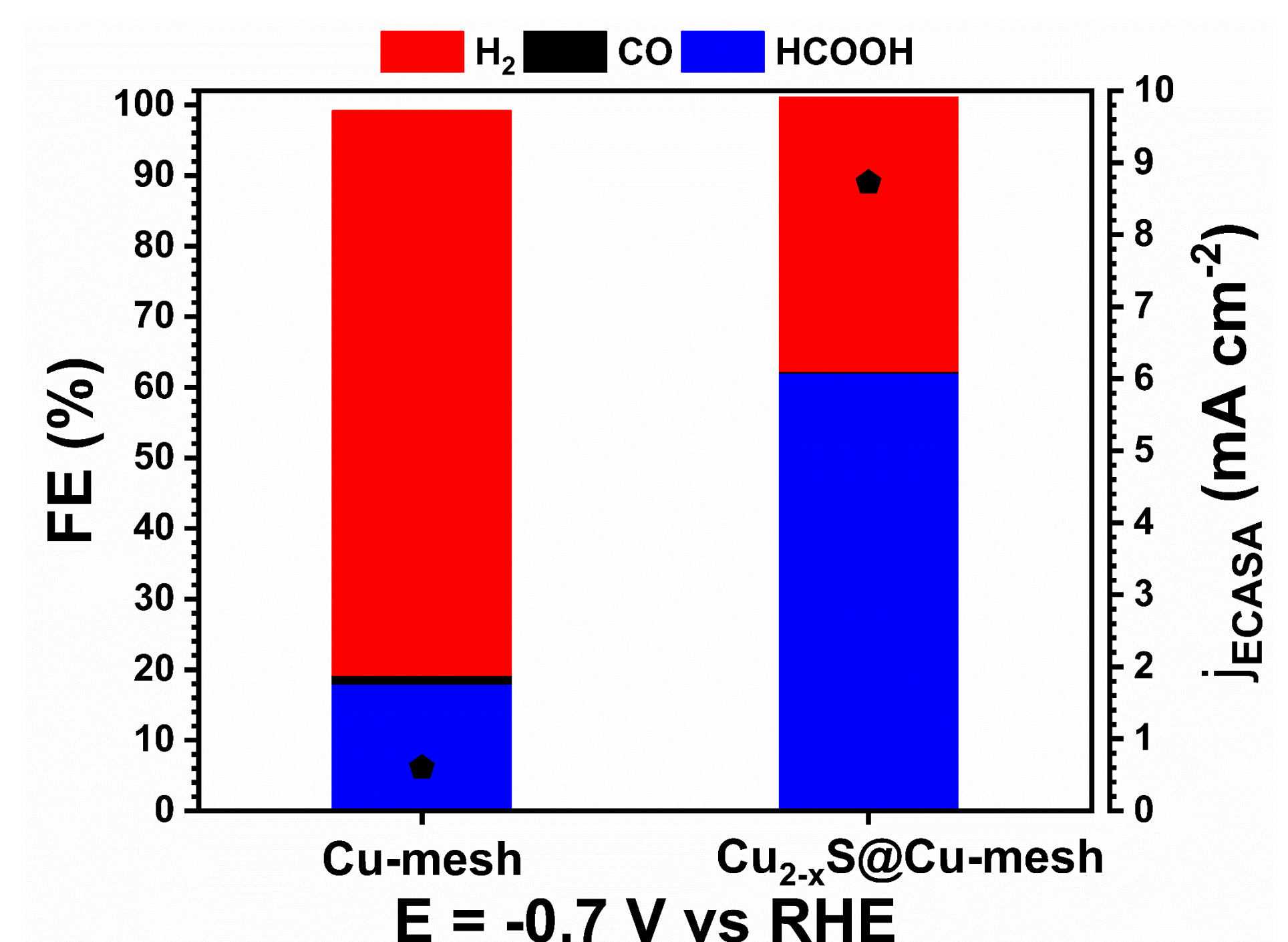
Synthesis and characterization of the Cu_{2-x}S



Electrochemical conversion of CO₂ into HCOOH on Cu_{2-x}S as catalyst



- The presence of sulfur on the Cu-surface enhances the selectivity towards production of HCOOH most probably due to changes in the CO₂⁻ intermediate binding mode from carbophilic into oxophilic



- Under CO₂ electrolysis condition, flower-like structures emerge from the Cu_{1.8}S coating