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ETRI 2023

BOOK OF ABSTRACTS

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conclusions are preliminary in nature. Further, in-depth research is required to comprehensively explore the geopolitical ramifications and practical applications of energy storage technologies, including electric cement. Additional data, analysis, and real-world implementation will provide a more comprehensive understanding of their role in the ongoing global energy transition and sustainability efforts.

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Abstract Title: Mechanistic insights of the plasmon-enhanced CO2 reduction reaction

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Abstract: This ongoing work discusses the use of Cu2O-Au semiconductor-metal composites in the electrochemical CO2RR to produce value-added chemicals and address climate change issues. The study explores different morphologies of Cu2O materials decorated with Au nanoparticles and evaluates their electrochemical performance using various techniques, including 3D printed electrochemical cells and online Electrochemical Mass Spectrometry (EC-MS). The addition of Au appears to enhance the reduction of Cu2O in light conditions, reducing

overpotential and increasing charge transfer. The Cu2O Au materials exhibit greater selectivity for certain CO2RR products, such as CO and C2H4, over CH4. In situ FTIR Reflectance Absorption Spectroscopy (FTIR-RAS) experiments revealed that a completely different mechanism is observed in each condition, providing insights into the influence of hot carriers in the CO2RR mechanism, with light incidence breaking strongly bonded H2O molecules.

Keywords: CO2, CO2RR, carbon dioxide, electrocatalysis, electroreduction, plasmonics, LSPR.

Introduction and Objectives: High carbon dioxide (CO2) emissions are attributed as the main cause of climate change, which has far reached consequences that impact the displacement of communities and loss of biodiversity. Changing weather patterns can disrupt agriculture and lead to economic challenges. As such, one strategy to both mitigate CO2 emissions and produce value-added chemicals is the electrochemical CO2 reduction reaction (CO2RR). Cuprous oxide (Cu2O) electrocatalysts are known to be amongst the most selective for C2 chemicals (ethanol, ethylene, amongst others) production through the CO2RR. It is also possible to fine-tune the material's surface to a given preferential exposed facet and control the morphology between cubic and octahedral, as CO2RR's intermediates adsorb differently depending on the availability of active sites, partially favouring a certain mechanistic pathway.
Furthermore, the coupling of Cu2O materials with plasmonic nanoparticles, such as gold (Au), is a promising underexplored field that could boost the selectivity for C2 even further through a phenomenon called Localized Surface Plasmon Resonance (LSPR). Besides confined local heating and near-field enhancement, LSPR can be used to inject excited charge carriers ("hot electrons") generated by Au's interaction with electric fields into the conduction band of Cu2O. Au can also play a big role in generating excess carbon monoxide (CO), which can be captured and further reduced to other chemicals by the Cu2O. However, despite high efficiencies being reported in the literature, mechanistic understanding of the plasmon-enhanced CO2RR is limited, and as such, in-situ surface analysis is vital for improved molecular-level comprehension and development of optimized systems. This work synthesizes Cu2O materials of different morphologies (cubic and octahedral) decorated with Au nanospheres towards the conversion of CO2 into C2 chemicals using visible light irradiation, as well as performing online and in situ experiments to achieve mechanistic insights in the role of each variable influencing the selectivity of the CO2RR.

Methodology: Cu2O materials are synthesized in different morphologies by preparing a solution of copper chloride (II), sodium dodecyl sulphate, sodium hydroxide, and varying contents of hydroxylamine hydrochloride (HH). Higher contents of HH in the synthesis solution result in octahedra, while lower contents result in cubes. Au decoration is done by galvanic substitution of the as-prepared Cu2O materials, with the use of polyvinylpyrrolidone and chloroauric acid, resulting in a Cu2O-Au semiconductor-metal composite. The materials were characterized by several non-electrochemical techniques, such as Atomic Absorption Spectroscopy, Diffuse Reflectance and Transmission UV-Vis Spectroscopy, Fourier

Transformed Infrared (FTIR) Transmission Spectroscopy, Scanning Electron Microscopy, Transmission Electron Microscopy, and X-Ray Diffraction.
For the evaluation of the electrochemical performance of each material, custom-made 3D printed electrochemical cells were utilized depending on the application. Either a glassy carbon or carbon paper drop-casted with the Cu2O-Au materials were utilized as working electrode, a platinum (Pt) ring as auxiliary electrode and silver chloride (Ag|AgCl|KClsat) as reference electrode. The electrochemical characterization and peak reduction assignments were performed with triangular potential perturbations carried out by a bipotentiostat in a CO2-saturated potassium bicarbonate (KHCO3) 0.1 M solution. The online Electrochemical Mass Spectrometry (EC-MS) technique was utilized to follow real-time gaseous product generation (such as CO, ethylene, and methane) in the working electrode, and comparisons were made between exposed facet, presence of Au nanoparticles, and light irradiation. In situ FTIR Reflectance Absorption Spectroscopy (FTIR-RAS) was utilized for evaluating changes in the mechanism by following IR bands related to possible products and intermediates with the applied potential. Both techniques are not commonly coupled with plasmon-enhanced reactions.

Preliminary results: Electrochemical characterization of the Cu2O materials shows that Cu2O is partially reduced to Cu before the CO2RR, evidenced by a reduction peak during cathodic linear sweep voltammetry (LSV). This is corroborated by some works in literature as well. The addition of Au seems to reduce the overpotential and increase charge transfer. When illuminating the electrode, the overpotential for the Cu2O reduction is greatly reduced, which could be related to the filling of the conduction band. This effect is enhanced with the addition of Au, being an indication that Au is injecting electrons in the conduction band of the Cu2O and therefore more easily allowing electron transfers. During online EC-MS, results show that CH4 is greatly mitigated with the addition of Au, and the more favourable pathway shifts for the formation of CO, while C2H4 production is roughly similar. The synergy between Cu2O and Au was more pronounced while utilizing the cubic materials. This is in agreement with reported works that exhibit a preference for CO and C2H4 over CH4 production when the preferential exposed facet of the catalyst is 100 instead of 111. When illuminating the electrode, a decrease in production of CH4 is observed, while all other gaseous products have their generation increased. As such, plasmon enhancement might be related to a release of *CO intermediates instead of hydrogenation. This was observed in similar works which argue that local heating might be favouring CO desorption, which in turn increases availability of active sites and increases electrochemical current. Our work suggests that the employment of both Au and light irradiation broadens the potential range in which little to no CH4 production is observed, which can be interpreted as higher selectivity for certain products amongst the several possible products of the CO2RR.
More recently, our group has begun tests with plasmon-enhanced FTIR-RAS experiments. Very few works have attempted to elucidate the hot-carrier influence in the CO2RR mechanism. Preliminary results showed that the behaviour of interfacial H2O molecules is completely different in each condition for the cubic materials (“Cu2O/dark”, “Cu2O-Au/dark”, “Cu2O-

Au/light"), and a proper evaluation of each situation is still undergoing. In the "Cu2O/dark" condition, lower overpotentials result in negative absorbance of O-H stretching and H-O-H bending bands, suggesting H2O consumption, possibly related to CO2 adsorption and HCOOH generation. Similarly, the "Cu2O-Au/dark" condition shows similar behavior but with pronounced H bonding and C2 production indicators. In the "Cu2O-Au/light" condition, light exposure sharpens the signal for "ice-like" H2O, indicating the breakage of stronger H-bonds. Corroboratively, higher positive signals and increased interfacial pH suggest proton consumption and OH- formation, as observed through the CO32- adsorption band.

Preliminary conclusions: The electrochemical characterization of Cu2O materials, particularly in combination with Au, revealed significant insights into their behaviour during the CO2RR. The addition of Au appeared to enhance charge transfer and reduce overpotential, with even more pronounced effects observed when illuminated. This suggests that Au may inject electrons into the conduction band of Cu2O, facilitating electron transfers. Online EC-MS results indicated that the presence of Au mitigated CH4 production, favouring the formation of CO, especially in the case of cubic materials. The synergy between Cu2O and Au in promoting CO and C2H4 production over CH4 aligns with previous studies. Furthermore, plasmon enhancement, potentially related to the release of *CO intermediates, may contribute to this selectivity by favouring CO desorption and increasing active site availability. Additionally, preliminary plasmon enhanced FTIR-RAS experiments highlighted the distinct behaviour of interfacial H2O molecules, shedding light on potential pathways for CO2RR intermediates like HCOOH generation. Overall, these findings provide valuable insights into the mechanisms of the CO2RR, offering avenues for enhancing selectivity and efficiency in producing valuable chemicals from CO2. Further investigations are warranted to fully understand the hot-carrier influence and optimize these materials for practical applications.

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Abstract Title: Screening of Ionic Liquids for CO2RR using Molecular Dynamics
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Abstract: We used Molecular Dynamics to perform a screening of 18 Ionic Liquids of electrochemical importance. All of the ionic liquids were based on 6 phosphonium cations, which prevent parasite reactions from occurring, thus enhancing faradaic efficiency of the whole process. The 3 anions considered are of proven electrochemical capacity. The ILs ability to solubilize CO2 was evaluated using computational methods. Two of the best ionic liquids