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Study of Plasmon-Assisted CO_2 Electroreduction on Cu_2O-Au Nanostructures Towards C_2 Compounds Synthesis

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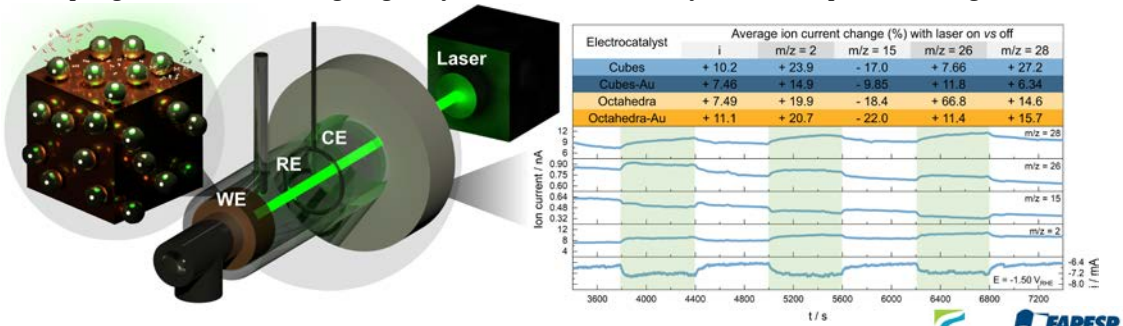
Allied to the growing global energy demand, the increase in the world average temperature due to continuous fossil fuels use brought impacting consequences to the planet. One strategy to tackle both issues is the electrochemical CO_2 reduction reaction (CO_2RR), which is a promising pathway to convert CO_2 into useful C_2 chemicals, such as 3rd generation ethanol, an important fuel to Brazilian energy matrix, and green ethylene. If the energy provided to the CO_2RR derives from sustainable sources, such as solar or wind power, it is possible to create a net-zero energy generation process. Despite being a well-researched reaction, there are still limitations that prevent its application on a large scale, mainly the low selectivity and operational current density. Cu-derived electrocatalysts are found to present the highest faradaic efficiency (FE) towards C_2 compounds due to its ability to more easily promote the C-C coupling at the surface. However, the numbers are still far from desired. Some of the strategies to favor the C-C coupling mechanism employ Cu_2O-derived electrocatalysts, creating defects at the surface (large number of grain boundaries) when reduced, as well as the presence of Cu^I nuclei adjacent to Cu^0. Moreover, the morphology and crystalline structure of the electrocatalyst can impact the selectivity due to the difference in adsorption energy of CO_2 between (100) and (111) exposed facets.

Another strategy not commonly found in the literature is the use of laser irradiation. Plasmon-assisted electrochemical reactions have been studied in the last decades as an approach to avoid macroscopic limitations, which consists in the use of mainly metallic nanoparticles, such as Au, whose electron clouds resonate with certain incident wavelengths, i.e. Localized Surface Plasmon Resonance (LSPR). The presence of LSPR phenomena allows reaction pathways that are not possible in purely electrochemical conditions or in non-nanostructured electrocatalysts, however, their enhancements to the CO_2RR are not yet fully detailed. The decoration of Au nanospheres over a Cu_2O particle results in Schottky-Junction processes, in which the hot electron generated at the Au nanosphere tunnels to the Cu_2O conduction band before being transferred to the adsorbed molecule. Furthermore, due to the semiconductor nature of the Cu_2O, the population of the conduction band with excited electrons from the valance band can also favor the electron transfer to the adsorbed molecule and, as such, one must be able to distinguish the plasmonic and semiconductor contributions to the selectivity of the CO_2RR.

This study combines the LSPR of Au nanospheres with the selectivity of Cu_2O-derived electrocatalysts, towards the plasmon-assisted CO_2RR. This presentation will discuss the characterization of each material and the results utilizing Mass Spectrometry coupled to electrochemical cell (EC-MS). Methane formation is greatly reduced when decorating the Cu_2O structures with Au, while carbon monoxide and ethylene production is increased. This corroborates with the mechanism that first the CO_2 is reduced at the Au nanosphere and then Cu_2O captures and further converts carbon monoxide to ethylene. When utilizing the laser (graphical abstract below), one can observe a similar phenomenon in which, upon irradiating the electrode with the laser, ethylene formation is being greatly favored over methane formation. The coupling of both these strategies greatly increase the selectivity for C_2 compounds during the CO_2RR.



Nat Energy, 2020, 5, 317 / Chem. Soc. Rev., 2014, 43 (11), 3898
ACS Energy Lett., 2019, 4 (5), 1098 / Appl. Catal. B Environ., 2020, 261, 118221

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