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Plasmonic Contributions to the CO_2 Reduction Reaction: An *In Situ* IR Spectroelectrochemical Study

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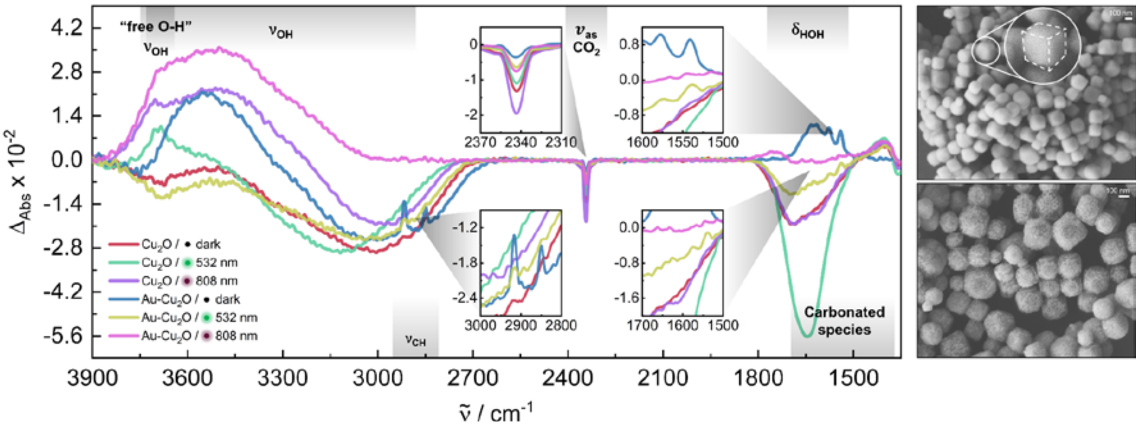
Anthropogenic CO_2 emissions are the primary driver of climate change. The electrochemical CO_2 reduction reaction (CO_2RR) is an approach to mitigate its atmospheric accumulation and create economic incentives for CO_2 sequestration. Despite being promising, the CO_2RR still presents limitations regarding the low selectivity towards alcohols and carbon chain molecules, in which Cu_xO_y-derived electrocatalysts ($x = 1, 2$ and $y = 0, 1$) are considered the best alternative. The combination of these materials with plasmonic nanoparticles (such as Au) is a strategy to both increase the production of CO and generate excited charge carriers through light-matter interactions at the nanoscale. However, few studies delve into the specifics of the charge transfer mechanisms occurring by plasmonic excitation of either Au and Cu, or the semiconductor properties of Cu_xO_y. Furthermore, the differentiation of enhanced activity by localized heating, hot electron injection, and how these contributions affect product selectivity is also lacking, and elucidating the dynamic changes in the interfacial electrolyte by *in situ* analysis is key for the development of better catalysts. Therefore, this study investigates the interfacial electrolyte structure of the aqueous plasmon-assisted CO_2RR by *in situ* FTIR, utilizing hybrid Cu_2O cubes (~ 300 nm) decorated with Au nanospheres (~ 30 nm), under illumination of two different wavelengths (532 nm and 808 nm).

The graphical abstract exhibits preliminary results for potential steps at -0.9 V_{RHE} for all conditions utilizing CO_2-saturated 0.1 M $KHCO_3$. A negative antisymmetric CO_2 stretch at 2343 cm^{-1} is observed, whose depletion with increasingly negative potentials indicates the decreased relative solubilized CO_2 concentration at the interfacial electrolyte relative to the open circuit potential (OCP) reference spectrum. The Au-decorated Cu_2O exhibited a smaller overall band area than the pure Cu_2O, which is opposite to what is expected. Wavelength effects were also significant: the 532 nm laser produced the lowest CO_2 depletion intensity in pure Cu_2O compared to 808 nm, while for Au-Cu_2O, CO_2 concentration remained similar to the OCP even under illumination. While these observations initially suggest a more sluggish consumption of CO_2, product quantification analysis indicates that the CO_2RR/HER selectivity is favored for the Au-decorated material. Shifts in water bending and O–H stretching bands revealed initial H-bond breakage (negative absorbance at ~3000 cm^{-1}) followed by the formation of H-bonds (positive absorbance near 3500 cm^{-1}). Additionally, the emergence of “free O–H” modes (~3700 cm^{-1}) under specific illumination conditions implies that photothermal effects, rather than hot electron transfer, drive increased activity observed for pure Cu_2O, while in Au-Cu_2O excited electrons promoted by the 532 nm laser appear to more easily reduce adsorbed $^*CH_2OH$ intermediates to CH_3OH. Finally, the detection of dual C–H stretching bands at 2849 and 2916 cm^{-1} observed solely in the Au-decorated material supports the formation of a $^*CH_2OH$ intermediate, correlating with increased alcohol selectivity.



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