In Situ ATR–SEIRAS of CO_2 Reduction at a Plasmonic Silver Cathode

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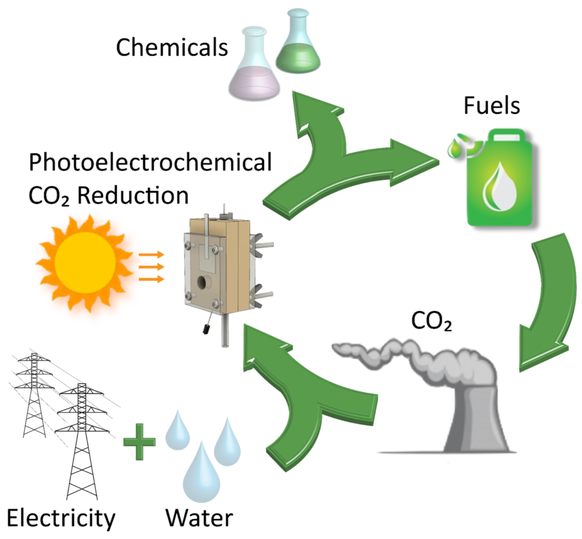
Inspiration

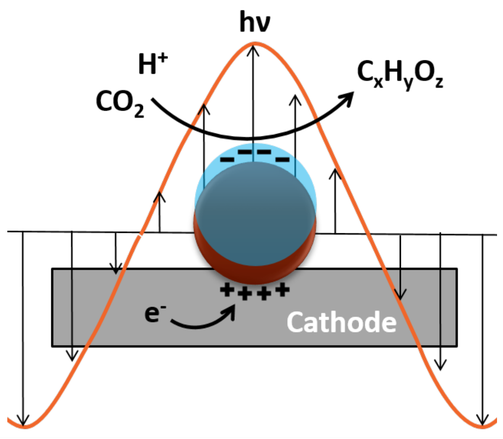
Goal: Convert Waste CO_2 into Fuels or Valuable Chemicals



Plasmonics

Plasmonic "Hot" Electrons for Catalysis

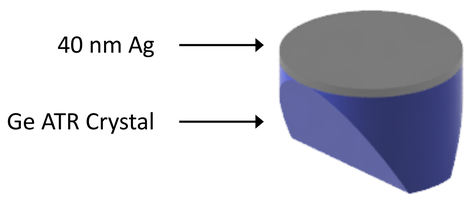
In a nanostructured metal, light can excite a plasmon, a collective oscillation of electrons. The plasmon decays to produce excited "hot" electrons that can influence chemical reactions.

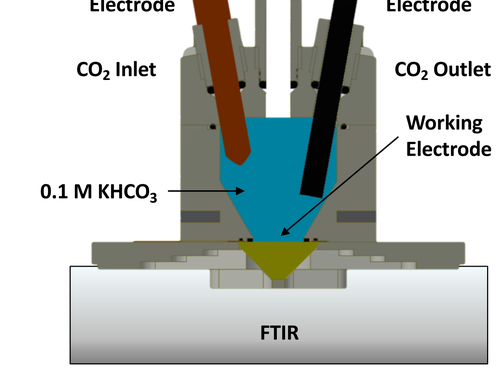


Photocathode

Synthesis of Silver Thin Film Photocathode

40 nm of silver is sputtered on a 60° germanium ATR crystal, forming the cathode. In situ attenuated total reflectance–surface-enhanced infrared absorption spectroscopy (ATR–SEIRAS) measurements probe species within 5–10 nm of the cathode surface during (photo)electrochemical CO_2 reduction.





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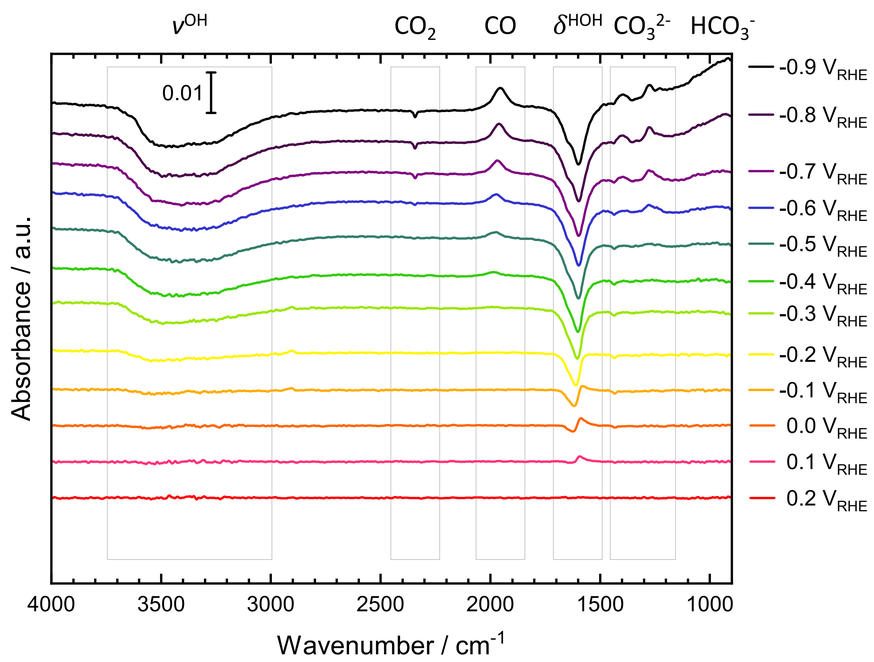
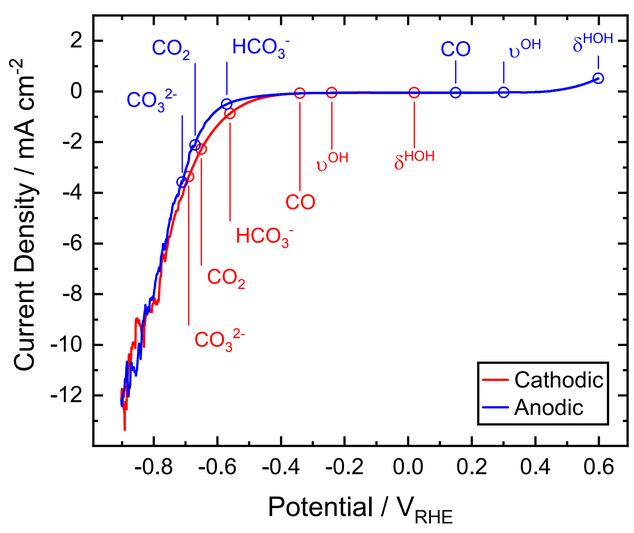
Species Detected During ATR–SEIRAS



0.1 M $KHCO_3$ • 30 sccm CO_2 flow • 2 mV s^{-1}

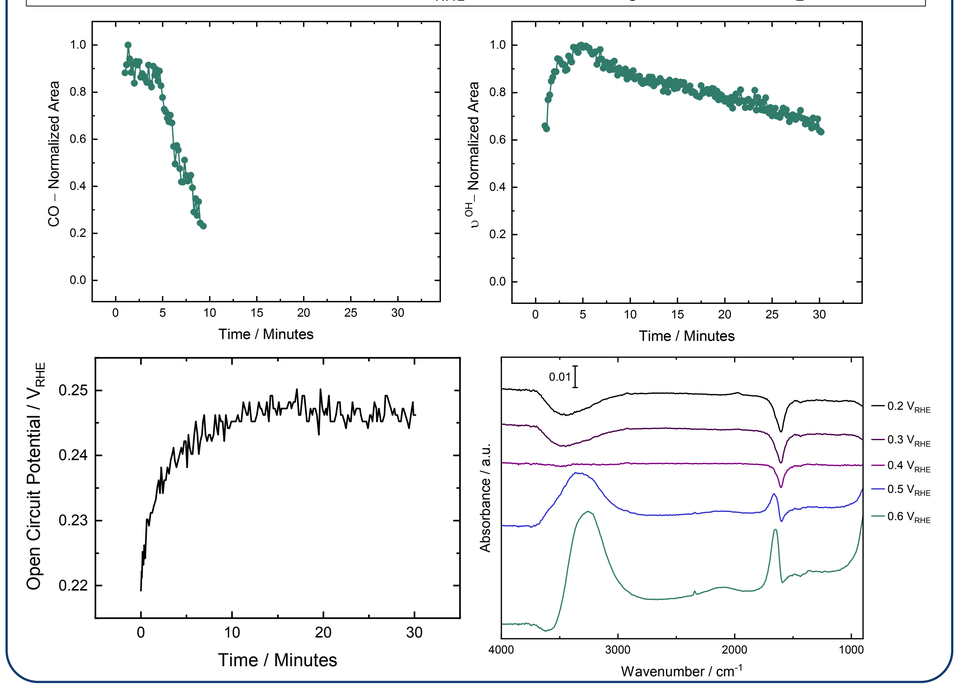


SEIRAS spectra were continuously measured during cyclic voltammetry. The peaks were identified as bicarbonate (HCO_3^-, 1278 cm^{-1}), carbonate (CO_3^-, 1395 cm^{-1}), water bending (δ^{HOH}, 1600 cm^{-1}), carbon monoxide (CO, 1970 cm^{-1}), carbon dioxide (CO_2, 2342 cm^{-1}), and water stretching (ν^{OH}, 3402 cm^{-1}).

The HCO_3^-, CO_3^-, and CO_2 peaks appeared and disappeared at the same potentials during cathodic and anodic scans. While the δ^{HOH}, CO, and ν^{OH} peaks appeared at 0.0 to -0.3 V_{RHE} on the cathodic scan, they did not disappear until 0.2 to 0.6 V_{RHE} on the anodic scan.

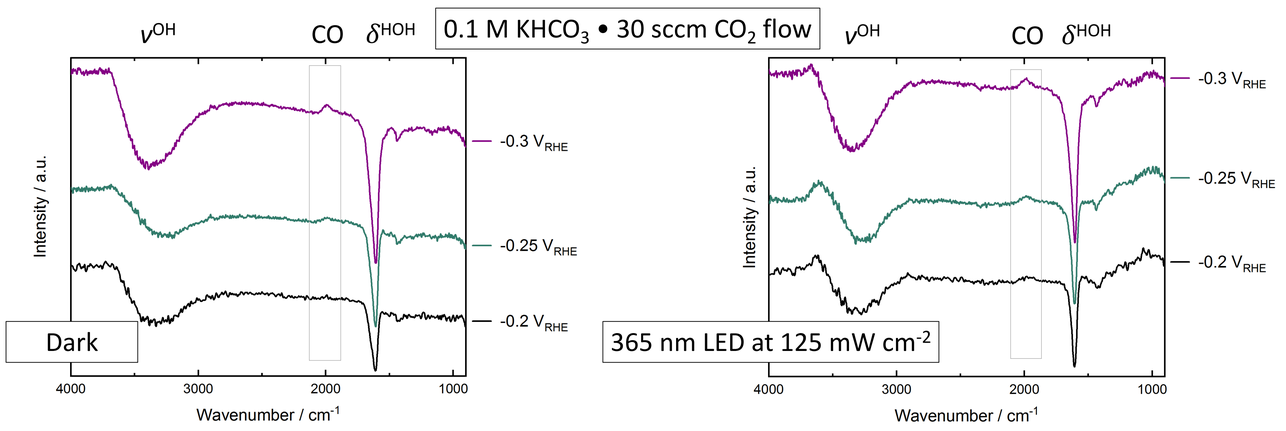
After 90 seconds at -0.6 V_{RHE}, CO remained on the surface for 10 minutes during open circuit potential (OCV) and the water peaks remained for more than 30 minutes. Anodic scans up to 0.4 V_{RHE} were performed after each experiment to "reset" the surface back to the baseline.

OCV after 90 seconds at -0.6 V_{RHE} • 0.1 M $KHCO_3$ • 30 sccm CO_2 flow

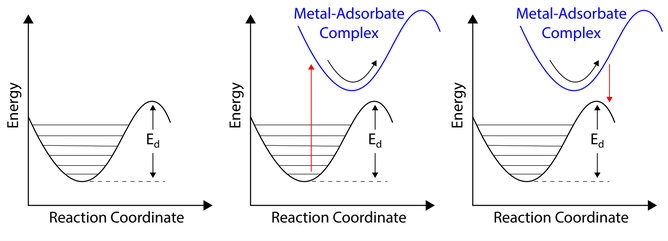


Light Enables CO Desorption

The onset of CO formation under illumination appears to be 300 mV less than in the dark during LSV. However, SEIRAS results show that CO is formed at the surface at -0.25 V_{RHE} in both the light and the dark. Thus, we conclude that the light is enabling CO desorption through the DIET mechanism.

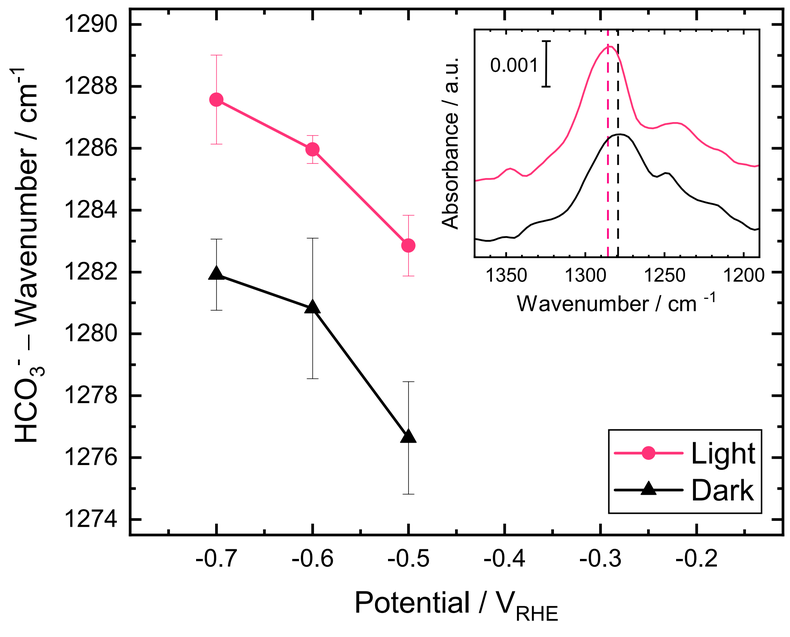


DIET Mechanism – Desorption induced by electronic transitions. A hot electron temporarily transfers to an unoccupied molecular orbital of an adsorbed species. After a few femtoseconds, the donated electron decays back to the metal Fermi level. If the energy transfer exceeds the activation barrier for desorption (E_d), the adsorbate will leave the surface.



Light Strengthens Bicarbonate Bond

0.1 M $KHCO_3$ • 30 sccm CO_2 flow • 365 nm LED at 125 mW cm^{-2}



Product analysis results show that CO production is enhanced in the light while H_2 evolution is suppressed at low overpotentials. SEIRAS results show that the HCO_3^- peak position increases by 6 cm^{-1} immediately upon illumination, signifying an increase in the bond strength. This would increase the local pH, leading to an enhancement in CO_2 reduction and diminished H_2 evolution.

The peak shift could be caused by interactions of HCO_3^- with the enhanced local electric field generated by the plasmon resonance.

Principal Investigators

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