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Plasmon-Driven CO2 Reduction via Hot-Electron Relay in Trimetallic Antenna-Reactor Catalysts: Mechanistic Insights and Reactor Design Principles

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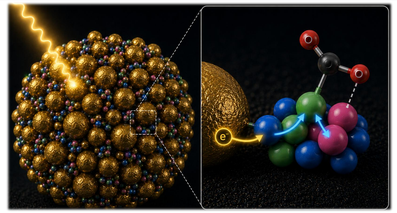
ABSTRACT and INTRODUCTION

The catalytic hydrogenation of CO_2 to CO via the reverse water-gas shift reaction provides a critical pathway for carbon valorisation, but conventional thermal methods face severe kinetic barriers. To bypass these limitations, we integrated a synergistic trimetallic active phase onto broadband-absorbing dendritic plasmonic colloidosomes (DPC-NiCoCu) to maximise visible-to-near-infrared light harvesting and promote intra-metallic electronic coupling. This architectural design achieves an exceptional CO production rate of 113 mmol g^{-1} h^{-1} with 100% selectivity. By coupling light-intensity-dependent kinetics with operando synchrotron HERFD-XANES and transient absorption spectroscopy, we demonstrate that copper acts as a conductive relay, directing hot electrons from the gold scaffold to the active nickel and cobalt centres. This directional routing induces a photon-flux-dependent mechanistic switch: at moderate flux, hot-electron injection increases the active site population to accelerate the rate without altering the thermal activation barrier, whereas high flux drives direct electron transfer into CO_2 antibonding orbitals, cutting the activation energy in half. Concurrently, in situ DRIFTS confirms that plasmon-induced desorption prevents surface poisoning, while a vertical temperature gradient across the catalyst bed promotes thermophoretic product removal, establishing a unified framework that links ultrafast hot-electron dynamics directly with reactor-scale transport.



SYNTHESIS AND CHARACTERISATION

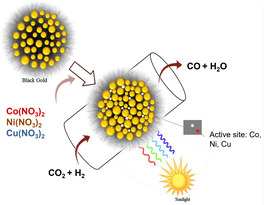


Fig 1: Synthesis of DPC-NiCoCu

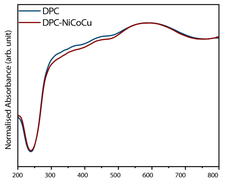


Fig 2: UV-DRS of DPC and DPC-NiCoCu

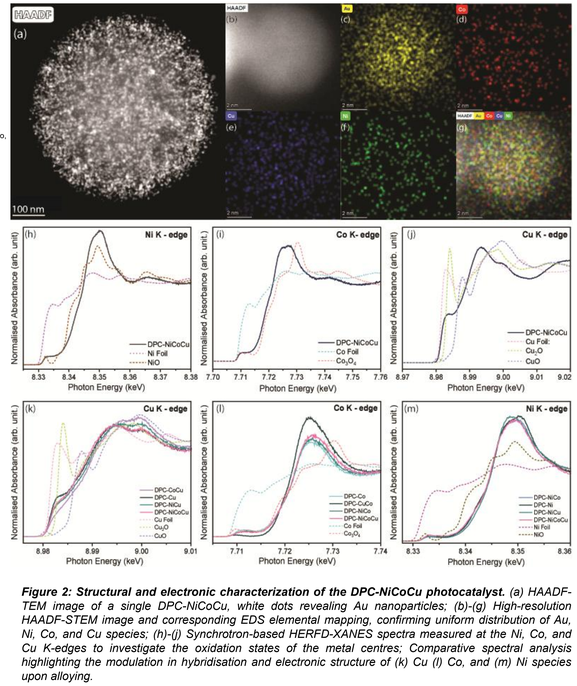


Figure 2: Structural and electronic characterization of the DPC-NiCoCu photocatalyst. (a) HAADF-TEM image of a single DPC-NiCoCu, white dots revealing Au nanoparticles; (b)-(g) High-resolution HAADF-STEM image and corresponding EDS elemental mapping, confirming uniform distribution of Au, Ni, Co, and Cu species; (h)-(j) Synchrotron-based HERFD-XANES spectra measured at the Ni, Co, and Cu K-edges to investigate the oxidation states of the metal centres; Comparative spectral analysis highlighting the modulation in hybridisation and electronic structure of (k) Cu (l) Co, and (m) Ni species upon alloying.

- **HAADF-STEM:** Uniform dispersion of trimetallic species without discrete large nanoparticles.
- **Oxidation States:** HERFD-XANES identifies metallic Au alongside hybrid Ni/Co/Cu redox states.

CATALYSIS PERFORMANCE and KINETIC ANALYSIS

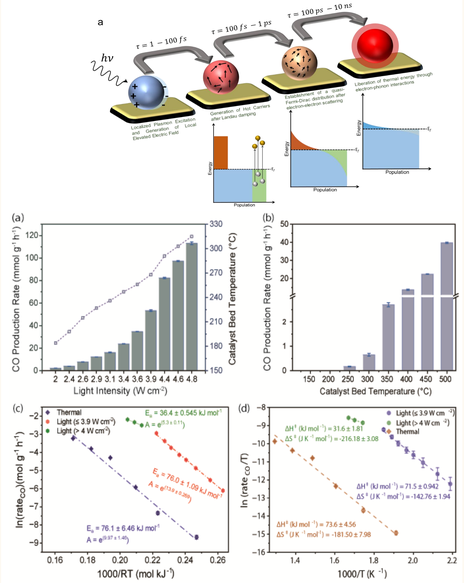


Figure 3. Photocatalytic CO_2 reduction performance and kinetics of DPC-NiCoCu. (a) CO production rates and catalyst temperatures under varying light intensities. (b) Dark thermal controls at varying temperatures. (c) Arrhenius and (d) Eyring plots under light and dark conditions.

CHARGE TRANSFER DYNAMICS

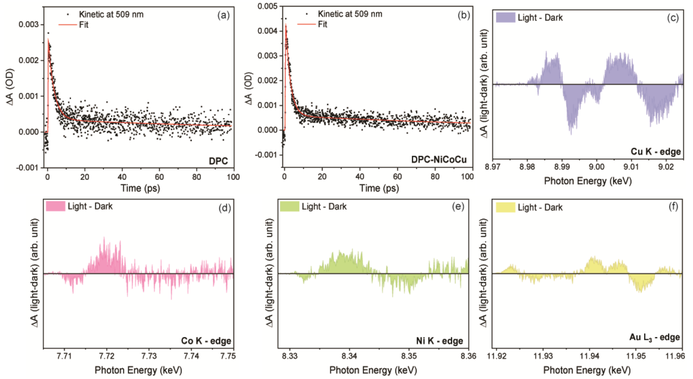
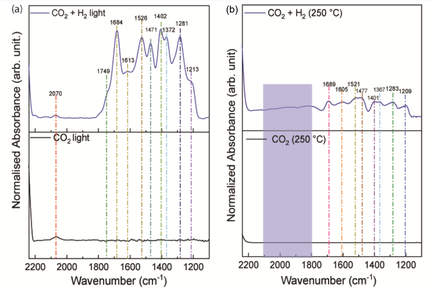


Figure 4. Mechanistic investigation of plasmonic hot-electron transfer. *(a) and (b) Kinetic traces extracted at the winglet maximum for DPC and DPC-NiCoCu, respectively; Difference XANES spectra illustrating the difference between the light on and light off states, (c) Cu K-edge, (d) Co K-edge, (e) Ni K-edge, and (e) Au L_3-edge..*

REACTION MECHANISM



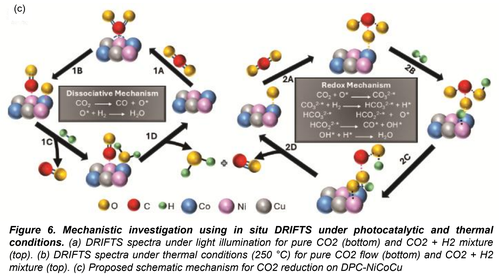


Figure 6. Mechanistic investigation using in situ DRIFTS under photocatalytic and thermal conditions. *(a) DRIFTS spectra under light illumination for pure CO2 (bottom) and CO2 + H2 mixture (top). (b) DRIFTS spectra under thermal conditions (250 °C) for pure CO2 flow (bottom) and CO2 + H2 mixture (top). (c) Proposed schematic mechanism for CO2 reduction on DPC-NiCoCu*

TRIMETALLIC COOPERATIVITY AT THE ACTIVE SITES

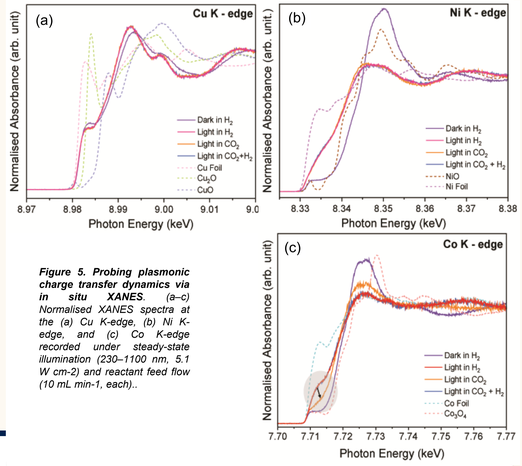


Figure 5. Probing plasmonic charge transfer dynamics via in situ XANES*. (a–c) Normalised XANES spectra at the (a) Cu K-edge, (b) Ni K-edge, and (c) Co K-edge recorded under steady-state illumination (230–1100 nm, 5.1 W cm-2) and reactant feed flow (10 mL min-1, each)..*

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CONCLUSION

- DPC–NiCoCu achieves 113 mmol g^{-1} h^{-1} CO production with 100% selectivity under ambient pressure without external heating.
- Light-intensity-dependent kinetics reveal two distinct regimes:
  - Moderate flux: Hot electrons activate additional surface sites.
  - High flux: Direct hot-electron transfer lowers the activation barrier and changes the reaction pathway.
- Ultrafast TAS and in situ HERFD-XANES confirm efficient plasmon-induced charge transfer from Au to the trimetallic active sites.
- A Cu-mediated charge relay creates electron-rich Ni and Co centres that enhance CO_2 activation.
- In situ DRIFTS shows hot-carrier-assisted CO desorption, suppressing catalyst poisoning and improving stability.
- This work provides a blueprint for designing high-performance plasmonic photoreactors for solar-to-fuel conversion.