Photocatalytic CO_2 Hydrogenation by "Hot Electrons" of Plasmonic Black Gold-Nickel

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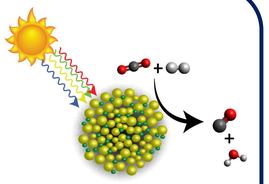
Introduction and Objective

CO_2 hydrogenation with green hydrogen can provide us an edge in the battle of climate change[1]. However, the high thermodynamic stability of the CO_2 molecule makes this process challenging. Thermocatalytic CO_2 hydrogenation needs high temperatures, causing quick deactivation of catalyst due to active site sintering and coke formation. The question that we asked is whether this reaction could be carried out at a reasonable temperature with the help of plasmonic light excitation.

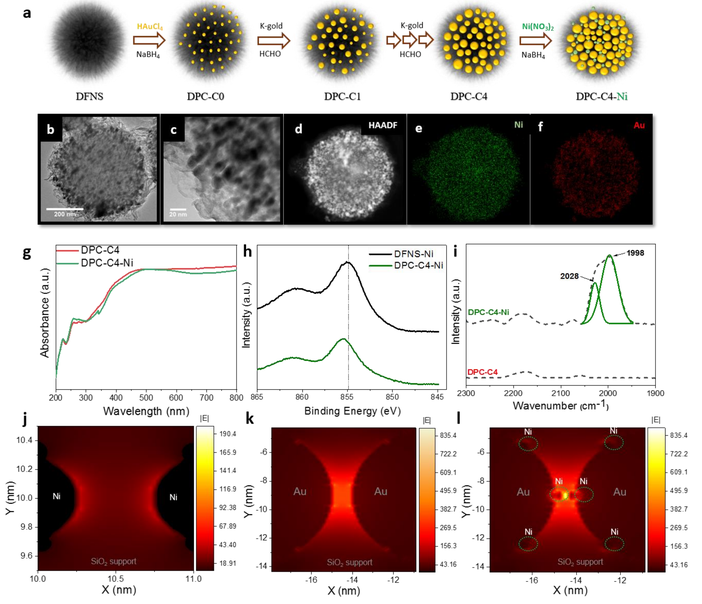
Plasmonic materials have unique ability to harvest light energy by coupling their electron density with the electromagnetic radiation of a specific wavelength (localized surface plasmon resonance, LSPR). [2,3] Plasmonic "antenna-reactor" catalyst designs provided magnificent catalytic activity, but antennas that are used in all these reported systems are conventional plasmonic metal nanoparticles with the limited light-harvesting ability of a specific narrow band wavelength. Ideally, the antenna should be a plasmonic material that can absorb the entire broadband solar spectrum so that more photons get harvested and, in turn, generate more hot spots and the maximum number of hot electrons, both of which can be used for catalysis.

In this work, we have designed dendritic plasmonic colloidosomes of Au (DPC-C4) also known as "black gold"[4] loaded with nickel sites (DPC-C4-Ni), prepared by loading four cycles of Au NPs on dendritic fibrous nanosilica (DFNS)[5,6]. Under light excitation, DPC-C4-Ni outperforms DPC-C4 and DFNS-Ni in terms of photocatalytic CO_2 hydrogenation activities. DPC-C4-Ni shows a very high photocatalytic CO production rate (2464 ± 40 mmol g_{Ni}^{-1} h^{-1}) with 95 % CO selectivity. The photocatalyst was stable for 100 h.

The photocatalytic CO_2 hydrogenation mechanism was explored by using i) finite-difference time-domain simulations (FDTD), ii) light intensity-dependent production rate, and iii) in-situ Diffuse Reflectance Infrared Fourier transform spectroscopy (DRIFTS) study. DRIFTS indicated the direct dissociation of CO_2 as the CO_2 hydrogenation mechanism via linearly bonded Ni-CO intermediates.



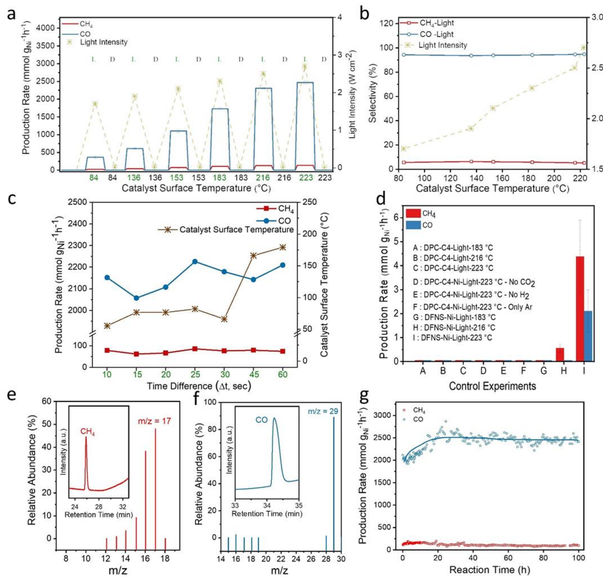
Synthesis and Characterization



(a) Schematic illustration of the synthesis process of DPC-C4-Ni; TEM images of (b, c) DPC-C4-Ni; (d-f) STEM-EDS elemental mapping of DPC-C4-Ni; (g) Absorption spectrum of DPC-C4 and DPC-C4-Ni; (h) Ni 2p XPS spectra expanded in the region of Ni $2p_{3/2}$, (h) DRIFTS spectra of CO adsorbed on DPC-C4 and DPC-C4-Ni. Electric field intensity in (j) DFNS-Ni, (k) DPC-C4, and (l) DPC-C4-Ni, using FDTD simulation.

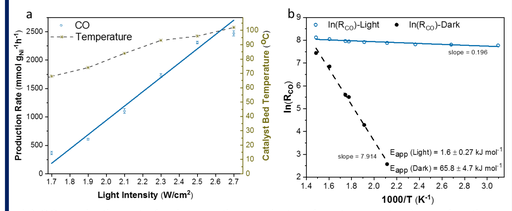
Plasmonic CO_2 Hydrogenation

Photocatalytic CO_2 Hydrogenation



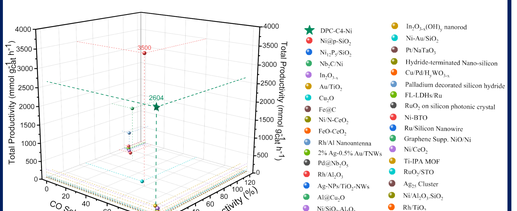
(a) Production Rate and (b) selectivity in light (no external heating) at various intensities and dark at different temperatures: H_2 (1 ml min^{-1}), CO_2 (10 ml min^{-1}), 400-1100 nm using Xenon lamp; (c) Production rate and catalyst surface temperature as a function of product sampling time difference (Δt), (d) Various Control experiments; ; Mass spectra of (e) $^{13}CH_4$ and (f) ^{13}CO, obtained using labeled $^{13}CO2$ as feed; (g) Long term stability study under the flow condition using light without external heating.

Activation Energy: Dark vs. Light

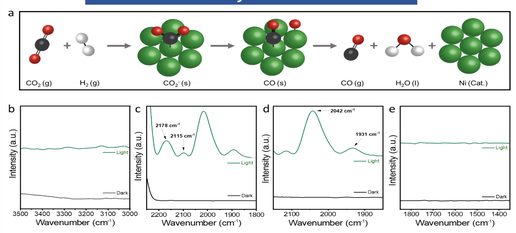


(a) CO production rate (and respective catalyst surface temperature) as a function of light intensity; (b) Arrhenius plot for activation energy calculation in dark and in light.

Catalysts Comparison



Mechanism by *in-situ* DRIFTS



(a) CO_2 hydrogenation mechanism via direct dissociation; FT-IR spectra with peaks for (b) methane, (c) gaseous CO, (d) adsorbed CO, and (e) adsorbed formate species.

Conclusions

- In this work, we have demonstrated that plasmonic black gold-nickel efficiently catalyzes CO_2 hydrogenation using visible light. The reaction took place as low as 84 to 223°C without external heating.
- It showed the best-reported CO production rate of 2464± 40 mmol g_{Ni}^{-1} h^{-1} and selectivity greater than 95% in the flow conditions. The catalyst showed extraordinary stability (100 h).
- In-situ DRIFTS study showed C=O stretching vibrations of linearly bonded CO atop Ni atom, while bridge carbonyl species formation was hindered. CO_2 hydrogenation took place by direct dissociation path via linearly bonded nickel-CO.

References

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Acknowledgements

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