Application Note

Keywords: Photocatalysis, Plasmonics, Energy conversion, Advanced spectroscopy

Revealing Hot-Electron Dynamics in Plasmonic Nanohybrids Using XPS and HAXPES

Depth-Resolved Chemical Insight into a CO2-Reducing Plasmonic Photocathode

Introduction

Understanding how charge carriers move across buried interfaces is central to developing next-generation systems for light-driven chemical transformations. In a recent study, Dey et al. Demonstrated that plasmon-generated hot electrons – rather than photothermal effects – directly drive the photoelectroreduction of CO2 to CO in a NiO/Au/ReI(phen-NH_2)$(CO)_3$Cl nanohybrid system.

One of the major challenges in verifying true hot-carrier involvement is the ability to probe chemical states and electronic interactions within multilayer architectures, where catalytic components sit beneath nanoparticles or oxide overlayers. This requires spectroscopic techniques capable of looking deeper under the surface while preserving chemical specificity.

To address this, the authors used both conventional X-ray Photoelectron Spectroscopy (XPS) and Hard X-ray Photoelectron Spectroscopy (HAXPES) in the Scienta Omicron HAXPES Lab. Together, these techniques provided complementary surface- and bulk-sensitive, non-destructive chemical analyses that confirmed the spatial arrangement, oxidation states, and electronic coupling required for ultrafast hot-electron transfer.

Objectives

- Demonstrate that plasmon-generated hot electrons in a NiO/Au/Re nanohybrid drive visible-light CO2 reduction to CO.
- Distinguish true non-thermal hot-carrier effects from thermal or non-plasmonic contributions.
- Validate the buried catalyst-metal-oxide architecture necessary for hot-electron transfer.

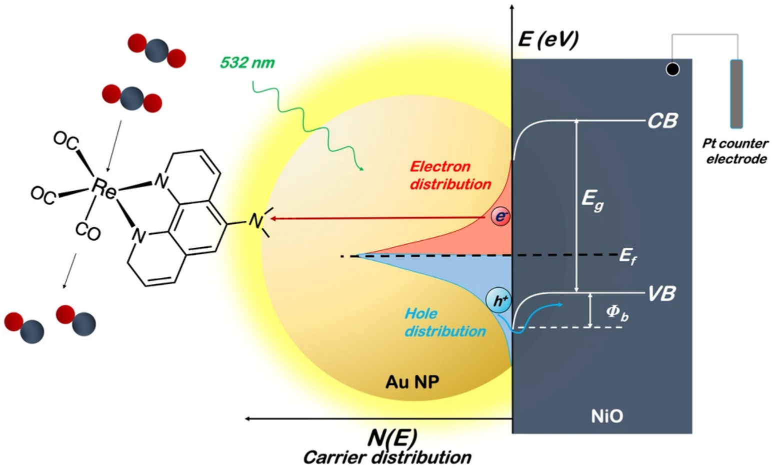

Fig 1: Schematic illustration of the NiO/Au/ReI(phen-NH_2)$(CO)_3$Cl nanohybrid used for photoelectrocatalytic CO_2 reduction.

Methods

Thin-film photoelectrocatalytic systems were fabricated on flourine-doped tin oxide (FTO) substrates, consisting of a NiO layer, Au nanoparticles, and a rhenium carbonyl complex catalyst anchored via its amine ligand.

To probe chemical composition, oxidation states and depth distribution, the following measurements were performed: **Al Kα (1.48 keV) XPS** for surface-sensitive analysis of the outer nanometers, and **Ga Kα (9.25 keV) HAXPES** for bulk-sensitive HAXPES probing tens of nanometers into the film.

Key Advantages of Combining XPS and HAXPES

1. Depth-resolved chemical insight
   XPS and HAXPES together reveal how elements are distributed from the surface into the film, confirming that Au and Re sit at the NiO interface as designed.

2. Verification of nanostructure architecture
   The depth-dependent signal changes directly validate the intended spatial arrangement of the catalyst and plasmonic nanoparticles.
3. Clear identification of oxidation states and bonding
   High-quality XPS spectra show metallic Au, Re(I), and surface-reduced NiO, while also confirming Au–N bonding between the catalyst and nanoparticle.
4. Non-destructive analysis of sensitive materials
   Both techniques probe chemical states without damaging the thermally sensitive Re complex, ensuring reliable characterization of the hybrid system.

Results and Discussion

XPS and HAXPES together provide a clear depth resolved view of the nanohybrid structure. With increased probe depth, the relative decrease of Au 4f and Re 4f signals compared to Ni and O confirms that the Au nanoparticles and the Re catalyst reside at or near the NiO surface. This matches the intended architecture shown in Fig. 1. The measurements also reveal the expected chemical states — metallic Au, Re(I), and a partially reduced NiO surface — along with shifts in N 1s and carbonyl features consistent with Au–N bonding. These findings demonstrate that the catalyst is successfully anchored to the plasmonic nanoparticles and electronically coupled to the surrounding oxide matrix.

This validated structural picture aligns with the authors' optical and electrochemical data, which together show that charge transfer within the hybrid proceeds through plasmon generated hot electrons rather than thermal pathways. The confirmed colocation and electronic connection between Au and Re, combined with the ability of NiO to extract holes and suppress recombination, support a mechanistic model where hot carriers are efficiently directed into the CO_2 to CO conversion cycle.

Conclusion

The XPS and HAXPES capabilities of the Scienta Omicron HAXPES Lab were essential for validating the electronic coupling and depth-resolved architecture of the plasmonic nanohybrid, which in turn enabled the authors to unambiguously attribute CO2 reduction activity to hot-electron transfer.

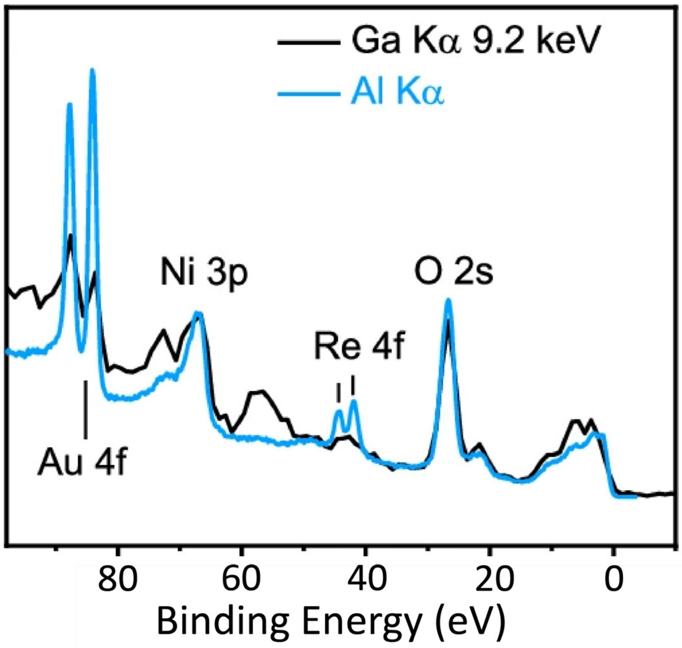

Fig 2: XPS (Al Kα) and HAXPES (Ga Kα) of the NiO/Au/ReI(phen-NH2)(CO)3Cl film.

Recommended For

- Researchers in photocatalysis, solar fuels, and plasmonic chemistry.
- Materials scientists developing multilayer thin films or hybrid nanostructures.
- XPS and HAXPES users who require depth-resolved chemical information beyond the limits of conventional XPS.

Reference:

Dey, A. et al, 2024. Commun Chem 7, 59.
https://doi.org/10.1038/s42004-024-01149-8

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