Application Note

Keywords: Energy storage, Catalysis, and Sensing

Surface Characterization of Mesoporous NiOx Using Ga Kα HAXPES

Differentiating Bulk and Surface Chemistry using HAXPES and AP-XPS

Introduction

Nickel oxide is a versatile transition-metal oxide, widely studied for applications in catalysis, energy storage, and electrochemistry, where surface states and their interaction with gases critically determine functionality. Disentangling bulk and surface contributions, however, remains challenging with conventional spectroscopic tools.

By combining surface sensitive, synchrotron, ambient-pressure (AP) XPS with lab-based, bulk-sensitive Ga HAXPES, this work disentangles the two. The authors show that mesoporous NiO surfaces are a dynamic mix of hydroxides and reactive oxygen species dependent on temperature, atmospheric oxygen and water. HAXPES provides the bulk reference needed to isolate subtle surface fingerprints, offering a powerful route to track how NiO surfaces respond under realistic conditions

Objective

To distinguish and quantify surface and bulk chemical states in mesoporous NiOx during thermal treatment and gas exposure, and to determine how surface hydroxides and oxygen species impact electronic properties.

Methods

Mesoporous NiOx films were characterized using:

- UV-vis and IR spectroscopy
- Synchrotron in situ AP-XPS for surface reaction sensitive measurements
- Laboratory Ga Kα HAXPES (9225 eV) for bulk-sensitive measurements

Key Benefits of Ga Kα HAXPES

1. Clear Isolation of Bulk NiO Signal

Ga Kα photons penetrate deeper into the sample (~tens of nanometers), minimizing surface sensitivity. The Ni 2p spectra obtained with Ga Kα reflect pure bulk NiO, with minimal interference from surface adsorbates. This signal serves as a baseline reference to subtract from soft X-ray AP-XPS data (Al Kα), which are surface-sensitive.

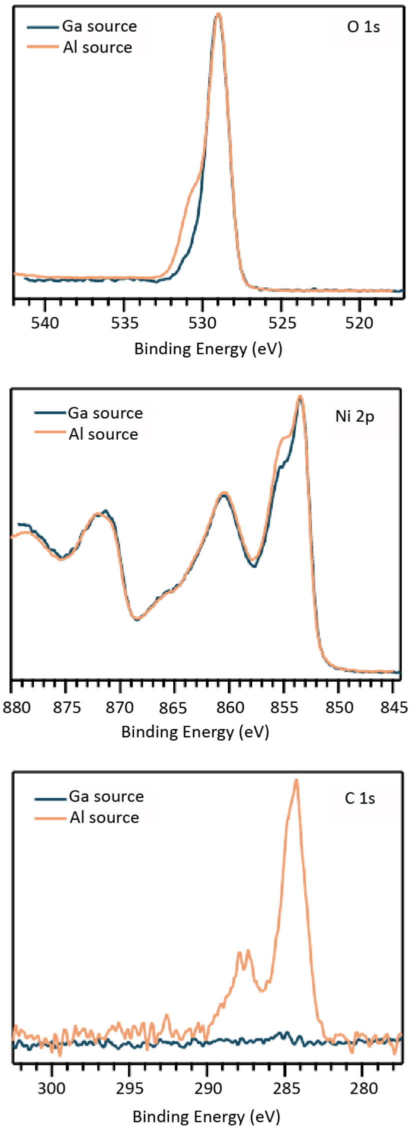

Fig 1: Spectra of NiOx films where the HAXPES reveals the bulk NiO spectrum compared to the surface sensitive XPS.

2. Surface Species Identification by Spectral Subtraction

By subtracting the Ga Kα-derived bulk spectra from surface-sensitive spectra, researchers could:

- Isolate surface Ni hydroxides, NiOOH, and Ni linked to oxygen adsorbates (O_2^-, O^-).
- Observe the thermal stability of different surface species.
- Identify temperature-sensitive Ni species such as those bound to water and weakly bound oxygen ions.

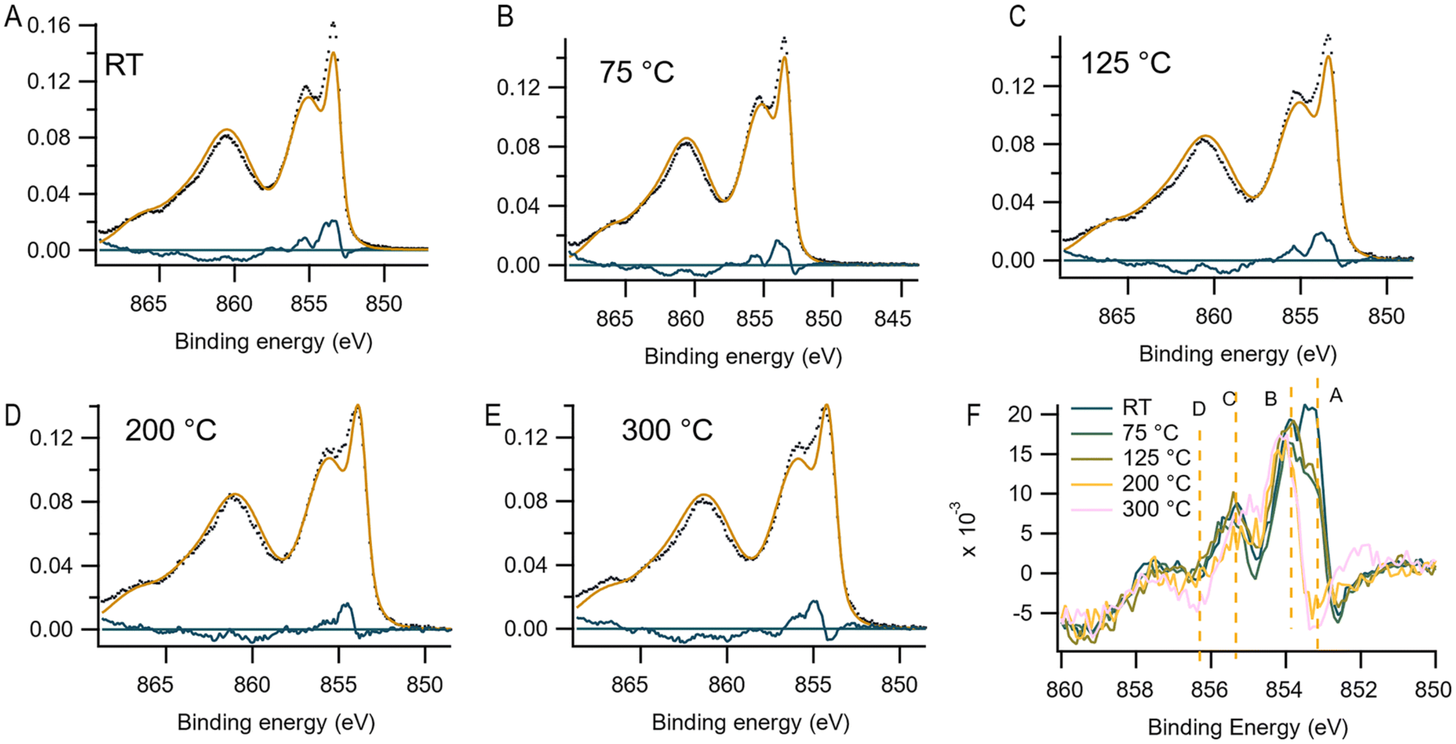

Fig 2: (A)-(E) Area normalized Ni 2p spectra of NiOx. Temperature dependent, surface sensitive synchrotron XPS spectra (black dots). By subtracting the HAXPES bulk spectrum (orange) a surface contribution comparison is realized in (F).

3. Complementarity with In Situ AP-XPS

While AP-XPS monitors real-time surface reactions under ambient pressures (e.g., during oxygen or water exposure), Ga Kα HAXPES anchors the analysis with a static, reliable bulk reference, enabling confident deconvolution of overlapping Ni 2p features.

Results & Insights

- Surface Ni species change significantly with temperature and gas environment.
- Surface oxygen ions (O_2^-, O^-) and Ni hydroxides dominate the active surface layer.
- These states can be reversibly removed or regenerated by Ar flow, heating, or oxygen exposure.
- Ga Kα HAXPES enabled accurate quantification of these changes and confirmed their absence in bulk.

Conclusion

Ga Kα HAXPES is a powerful tool for surface/bulk differentiation in complex metal oxide systems like NiOx. When combined with soft X-ray AP-XPS, it enables:

- High-resolution insight into surface chemistry
- Precise identification of functional species affecting electronic properties
- Improved understanding for the optimization of materials in real-world conditions

Recommended For

- Materials scientists studying porous or catalytic oxides
- Researchers optimizing surface states for sensors, solar cells, or batteries
- Users of HAXPES systems requiring deep chemical insight beyond surface-only analysis

Reference:

Wrede, S., Tian, H., et al. 2025. Phys. Chem. Chem. Phys. 27, 12762–12773.

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