

Unveiling Humidity-Enhanced Performance in Chemoresistive CoCu₂O₃ VOCs Sensors

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Summary:

Oxidation chemistry is centered around understanding the electron flow that involves reactants, products, and reaction-derived adsorbate species. In chemical sensing, this electron flow results in electrical conductivity modulations in a thin film of semiconductor (oxide) nanoparticles. Therein, understanding which surface-adsorbed species are electronically coupled to the material is crucial. Here, we develop a methodology that separates ionized from dipolar surface populations, to elucidate the unusual promoter effect of humidity on metastable, nanocrystalline CoCu₂O₃. Our results outline strategies to turn humidity from detrimental to a functional advantage in gas sensor performance.

Keywords: oxidation catalysis, cobalt-copper oxides, electronic properties, molecular sensor.

Background, Motivation and Objective

Understanding how electrons are transferred, stored, and redistributed during surface redox is central to metal oxides, widely deployed in chemoresistive gas sensing. Therein, even modest perturbations (e.g., oxygen vacancy population, surface adsorbates) can change adsorption properties and electron flow throughout a catalytic turnover. Such perturbation may arise from background molecules, most notably H₂O, omnipresent in realistic sensor scenarios. It is essential to develop strategies to render the performance of conventional sensing materials more humidity-tolerant, to achieve stable and long-term operation in ambient air (e.g., air quality monitoring [1]).

In chemoresistive metal-oxide gas sensors, reaction-derived surface species that are not ionized remain electrically neutral and act as surface dipoles mainly affecting electron affinity, whereas ionized vacancies and adsorbates contribute directly to band bending and charge-carrier populations. Investigating the effect of H₂O on such *ionized* vs. *dipolar* distribution is essential for addressing the humidity-induced inhibition of chemical sensors, e.g., ~3-fold response-reduction in 90% relative humidity (RH) [2]. In mixed transition metal oxides, redox chemistry and charge-carrier modulation may not be

confined to the same sites: one sublattice could be more directly involved in bond activation, whereas the other stabilizes ligand states that govern conductivity. Cobalt-copper oxides are an appealing platform to investigate these effects, owing to their rich valence chemistries that make them widely used in oxidation catalysis and gas sensing.

In this work, we employ CoCu₂O₃ as a mixed-oxide model system to unveil H₂O-induced modifications of receptor and transducer functions in a *p*-type semiconductor. To this end, we combined *operando* electrophysical measurements (DC resistance and work function), chemisorption analysis, and oxidation kinetics with surface-sensitive, *in situ*, near-ambient-pressure (NAP) X-ray photoemission and absorption spectroscopies.

Methodology

CoCu₂O₃ nanoparticles are fabricated by flame-aerosol technology as described in our previous work [3]. Chemoresistive films are obtained by direct flame-aerosol deposition on top of micro-fabricated substrates with interdigitated Pt electrodes and an integrated meander-shaped Pt resistive heater. These sensors are mounted onto MACOR® holders and placed in PTFE-made chambers, connected to a gas delivery manifold

comprising several thermal mass flow controllers. The resistance is measured between the interdigitated electrodes with a multimeter, and sensors' heating elements are heated to 200 °C via a DC power supply. For simultaneous work function (ϕ) measurements, the same MACOR®-supported sensor substrates are installed into aluminum chambers, with a hole drilling on the top that allows the Au tip (2 mm) of the Kelvin oscillator probe to approach the sample at working distances of approx. 0.5 mm. Temperature-programmed (TP) chemisorption characterization is performed to assess analyte-/oxidant-induced reactivity under either (i) dry or (ii) humid constant backgrounds.

The soft X-ray-based NAP spectroscopies are accomplished at the CAT@EMIL end-station of the Bessy II storage ring operated by the Helmholtz-Zentrum Berlin (HZB) für Materialien und Energie. Several reactive environments under different CO:O₂:H₂O and xylene:O₂:H₂O mixtures are obtained, at a total pressure of 1 mbar. X-ray photoemission (C and O 1s, Co and Cu 2p core levels) and absorption (O-K, Co- and Cu-L_{2,3} edges) spectra are recorded.

This combination of techniques allows to elucidate the electron flow [4]. In dry conditions, electrons from reducing molecules are exclusively allocated to O(2p)–Cu(3d) states, while building up a considerable fraction of carbonaceous species that are neutral, i.e., do not affect electrical conductivity but rather *trivially* shift electron affinity (χ). In the presence of humidity, despite slower lattice O²⁻-driven turnover, the removal of such carbonaceous dipoles is promoted, with up to approx. 50 meV χ -gains ($\Delta\chi_{\text{gain}}$). This has a significant influence on CoCu₂O₃ operated at 200 °C ($k_B T \approx 40$ meV), decreasing its ligand-hole concentration by a factor of $\exp\left(\frac{\Delta\chi_{\text{gain}}}{k_B T}\right)$.

In conclusion, electrons are re-routed from Cu(3d)-only ligand-hole states (sub-optimally allocated) to O(2p)–Co(3d), activating Co-redox and yielding enhanced conductivity modulations, i.e., sensor performance.

Results

We quantified the electronic modulation of Co and Cu in CO:O₂:H₂O mixtures. We focused on the evolution of Co valence inferred from its Co 2p envelope and the Cu⁺/Cu²⁺ balance, as shown in **Figure 1**, while gradually increasing CO partial pressure in an O₂ environment, in either (i) dry, (ii) 20% or (iii) 70% H₂O constant backgrounds. As can be observed, in dry

conditions, increasing CO pressure exclusively affects the Cu–O sublattice, with a growing Cu⁺ fraction, and unaltered Co-spin distribution (from Co L₃-NEXAFS, not shown), showing even a slight net oxidation.

On the other hand, under 20% and 70% H₂O, modest increments of CO pressure decrease the Co-2p-inferred valence. Therein, under humid conditions, the burden of oxygen-vacancy formation and associated electron uptake is redistributed across Co–O and Cu–O, harnessing rerouted electrons which were sub-optimally placed in electrophilic carbonaceous species.

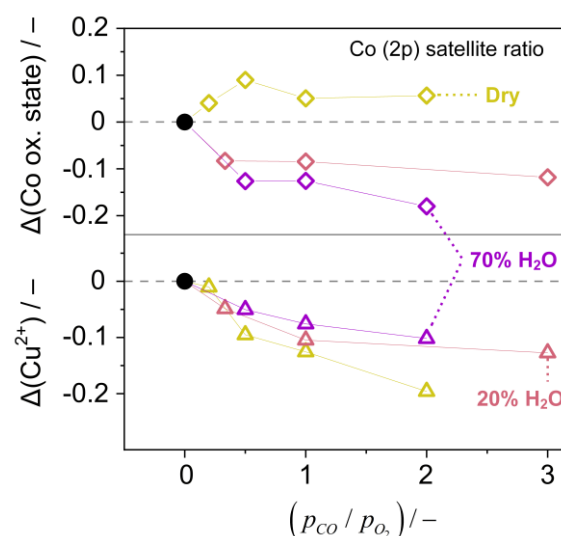


Fig. 1. Summary of CoCu₂O₃ evolution during CO dosing, starting from a CO-free baseline in either (i) dry, (ii) 20% or (iii) 70% H₂O backgrounds, showing the shift in Co oxidation state (inferred from Co 2p satellite analysis) and Cu²⁺ amount.

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