

Selective Formaldehyde Sensing: Unraveling Metal–Support Interaction Effects in Single-Atom Cu Catalysts

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Summary:

The selective detection of air pollutants remains a critical challenge. Here, we investigate the role of metal–support interaction in determining gas sensing behavior using single-atom Cu catalysts anchored on Co_3O_4 for formaldehyde vapor. Strong interfacial coupling modulates the redox properties of the support, enhancing sensitivity, selectivity, and low-temperature operation toward formaldehyde. This work provides mechanistic insights into how atomic-level catalyst–support integration governs environmental sensing performance.

Keywords: formaldehyde sensing, single-atom catalyst, Co_3O_4 , metal–support interaction, gas sensor mechanism

Background, Motivation and Objective

Detecting formaldehyde at trace concentrations is critical for indoor air quality monitoring. Chemoresistive gas sensors relying on semiconductive nanoparticles[1] are promising due to their compact size, low power and high sensitivity. While Co_3O_4 is a promising oxide for chemoresistive sensors, its performance is limited by poor low-temperature reactivity and selectivity.[2] Single-atom catalysts (SACs), when electronically coupled to the support, can modulate surface redox properties and enable more efficient gas-solid interactions.[3] Here, we investigate Cu-based SACs on flame-made[4-6] Co_3O_4 and directly compare them with nanoparticle-decorated counterparts. Our objective is to reveal how metal–support interaction (SMSI) at the atomic scale governs sensitivity, humidity stability, and gas selectivity in formaldehyde sensing.

Description of the New Method or System

Atomically dispersed Cu^{2+} species were stabilized on Co_3O_4 nanoparticles through a post-synthetic incorporation route, facilitated by intrinsic surface defects introduced during the oxide fabrication process. Spectroscopic analyses confirmed the formation of well-defined metal–oxygen–support interfacial motifs, accompanied by enhanced surface redox reactivity. This engineered interface led to a notable improvement in sensing performance under low-temperature and humid conditions, outperforming systems

based on aggregated Cu species or unmodified supports.

Results

H_2 -TPR analysis (Fig. 1) revealed a distinct low-temperature reduction peak in the Cu SAC system, indicating enhanced lattice oxygen activation due to strong metal–support interaction. Under 50% relative humidity, the Cu SAC sensor maintained the highest absolute response to 1 ppm formaldehyde among all samples (Fig. 2), demonstrating superior low-temperature activity and robustness under realistic environmental conditions

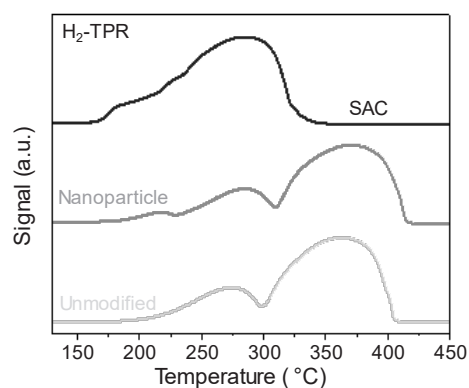


Fig. 1. H_2 -TPR profiles of pure Co_3O_4 , $\text{Cu}_{\text{NP}}\text{-Co}_3\text{O}_4$ and $\text{Cu}_1\text{-Co}_3\text{O}_4$ under 5 vol% H_2/Ar .

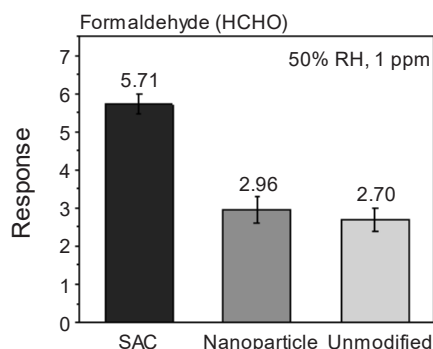


Fig. 2. Response of $\text{Cu}_1\text{-Co}_3\text{O}_4$ toward 1 ppm formaldehyde in comparison to reference samples at 50% RH and 75 °C.

References

- [1] P. M. Bulemo, D.-H. Kim, H. Shin, et al., Selectivity in Chemiresistive Gas Sensors: Strategies and Challenges, *Chemical Reviews* (2025); doi: 10.1021/acs.chemrev.4c00592
- [2] M. D'Andria, F. Krumeich, Z. Yao, et al., Structure-Function Relationship of Highly Reactive CuO_x Clusters on Co_3O_4 for Selective Formaldehyde Sensing at Low Temperatures, *Advanced Science* 11, 2308224 (2024); doi: 10.1002/advs.202308224
- [3] G. Lei, H. Pan, H. Mei, et al., Emerging Single Atom Catalysts in Gas Sensors, *Chemical Society Reviews* 51, 7260-7280 (2022); doi: 10.1039/D2CS00257D
- [4] A. T. Güntner, N. J. Pineau, S. E. Pratsinis, Flame-Made Chemoresistive Gas Sensors and Devices, *Progress in Energy and Combustion Science* 90, 100992 (2022); doi: 10.1016/j.pecs.2022.100992
- [5] M. D'Andria, T. E. A.-R. Silva, E. Consogno, et al., Metastable CoCu_2O_3 Nanocrystals from Combustion-Aerosols for Molecular Sensing and Catalysts, *Advanced Materials* 36, 2408888 (2024); doi: 10.1002/adma.202408888
- [6] A. Baut, M. P. Martins, A. T. Güntner, Template-Free Synthesis of Highly Porous Metal Nitride Architectures for Electronics and Molecular Sensing, *Small Structures*, 2500044 (2025); doi: 10.1002/ssstr.202500044

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