

Ensemble Nuclearity Optimum in Chemoresistive Hydrogen Sensing

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Summary:

Chemoresistive hydrogen sensing with Pd-functionalized oxides still depends largely on empirical optimization, as the atomic-scale descriptor governing performance remains unclear. Here, we establish ensemble-defined Pd motifs with controlled nuclearity (Pd1-Pd3) on a nanostructured oxide and identify a non-monotonic nuclearity-performance relationship with an intermediate ensemble as the optimum. Combined experiments and density functional theory calculations show that this trend originates from nuclearity-specific hydrogen adsorption and activation rather than oxygen-centered surface descriptors.

Keywords: hydrogen sensing, palladium nuclearity, Chemoresistive sensor, atomic ensembles, Predictive materials design

Background, Motivation and Objective

Pd functionalization is a common strategy to enhance oxide chemoresistors for hydrogen sensing,[1] but material selection and optimization remain largely empirical because the structural descriptor that predicts performance is still unclear. This limitation is particularly pronounced when Pd is distributed as heterogeneous surface species, where the contribution of discrete atomic ensembles cannot be isolated and a direct structure-performance relationship cannot be established.

This work addresses that gap by testing Pd nuclearity as a motif-resolved design variable for chemoresistive hydrogen sensing. The objective was to construct ensemble-defined Pd1, Pd2, and Pd3 motifs [2] on a flame-made nanostructured oxide,[3] verify their local structures using complementary experimental and computational methods, and determine how ensemble nuclearity governs hydrogen adsorption and activation and thereby controls sensor response, selectivity, and limit of detection.

Description of the New Method or System

We developed a structure-validated chemoresistive hydrogen sensing platform based on ensemble-defined Pd motifs with controlled nuclearity on a flame-made nanostructured oxide. Using a solution-phase functionalization strategy, discrete Pd1, Pd2, and Pd3 ensembles were introduced while preserving the support structure, enabling direct comparison of motif-dependent sensing behavior within a single material

system. The local structures of these Pd motifs were then validated by complementary spectroscopy, microscopy, and atomistic modelling, providing a rare platform in which the atomic configuration of the sensitizer is explicitly resolved rather than treated as a heterogeneous PdO_x decoration.

The methodological advance lies in combining motif-controlled synthesis, structure validation, mechanistic screening, and device-level comparison to identify Pd nuclearity as a predictive design variable for hydrogen sensing. Rather than attributing performance trends to generic oxygen-related effects, the system allows nuclearity-dependent hydrogen adsorption and activation to be isolated as the dominant differentiator. This establishes ensemble nuclearity as a practical motif-resolved descriptor and provides a general framework for predictive design of Pd-functionalized oxide chemoresistors.

Results

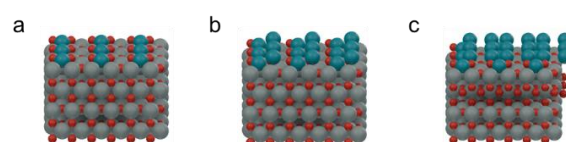


Fig. 1. Visual illustration of a) Pd1, b) Pd2 and c) Pd3 ensembles on a metal oxide support.

A structure-validated Pd nuclearity series was established on the flame-made nanostructured oxide, enabling direct comparison of Pd1, Pd2, and Pd3 motifs within a common support framework. Atomistic modelling identified distinct local

geometries and stabilization modes for each ensemble, and complementary structural characterization verified the targeted motifs, confirming that the sensing platform captures discrete Pd nuclearity as a controlled surface variable. This structural definition provides the basis for the observed performance trend and is summarized in Fig. 1, where the different Pd ensembles are represented as motif-resolved surface structures. Across the full sensing dataset, hydrogen response followed a clear non-monotonic dependence on nuclearity, with the intermediate ensemble consistently delivering the optimum performance over the measured temperature range, as reflected in the temperature-dependent sensor data shown in Fig. 2.

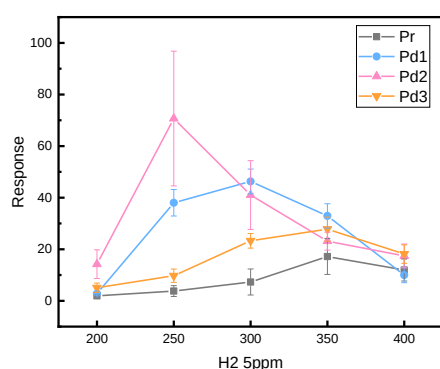


Fig. 2. Temperature-dependent chemoresistive hydrogen sensing performance of pristine oxide and the Pd-functionalized oxide sensors with controlled Pd nuclearity.

The origin of this nuclearity-dependent sensing behavior was then resolved by combining

mechanistic screening experiments with density functional theory calculations. Surface adsorbed oxygen species and surface lattice oxygen reducibility did not correlate with the sensor trend, excluding oxygen-centered descriptors as the dominant origin of performance differences in this system. H₂-temperature-programmed reduction and calculated hydrogen adsorption energetics identified a nuclearity-specific hydrogen adsorption and activation landscape, which explains why the intermediate Pd ensemble outperforms both the monomeric and trimeric motifs. This motif-resolved reactivity trend was consistent with the device-level comparison across response, selectivity against representative interferents, and limit of detection, establishing ensemble nuclearity as a practical descriptor for predictive chemoresistive hydrogen sensing.

References

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