

Polymorph-Dependent Electronic Transduction in WO₃ during Molecular Sensing through Experiment and DFT

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Summary:

Tungsten trioxide (WO₃) polymorphs have been widely studied for molecular sensing, yet the origin of their different chemoresistive behaviors remains unclear. Here, structural and spectroscopic characterization, in situ DRIFTS, and density functional theory (DFT) simulations reveal that both γ - and ϵ -WO₃ exhibit similar surface-level activation of acetone, whereas only ϵ -WO₃ stabilizes analyte-induced electronic states derived from W(5d) orbitals. These subsurface electronic rearrangements may explain its superior transduction efficiency despite similar receptor chemistry. Our findings provide a new framework for rational transducer design rooted in intrinsic electronic structure.

Keywords: WO₃, polymorphism, gas sensors, DFT, electronic structure

Background, Motivation and Objective

WO₃ is one of the most widely studied metal oxides for chemoresistive gas sensing. Besides the thermodynamically stable γ -phase, the metastable ϵ -WO₃ polymorph has shown higher responses, for example, toward acetone [1]. Despite its promising performance in advanced sensing applications, including non-invasive metabolic monitoring, the mechanistic origin of its superior response remains unclear. Conventional surface-chemical explanations based on adsorbate binding, oxygen activation, or intermediate speciation have not adequately explained the performance difference. In particular, the influence of crystal polymorphism on electron transfer and localized electronic states during molecular sensing remains largely unexplored. Here, using acetone as a model analyte, we investigate polymorph-dependent electronic transduction in WO₃ through a combined experimental and DFT approach.

Methodology

γ -WO₃ and ϵ -WO₃ nanoparticles were synthesized by the flame spray pyrolysis method. Structural characterization was performed by XRD, HR-TEM, XAFS, and XANES, while the

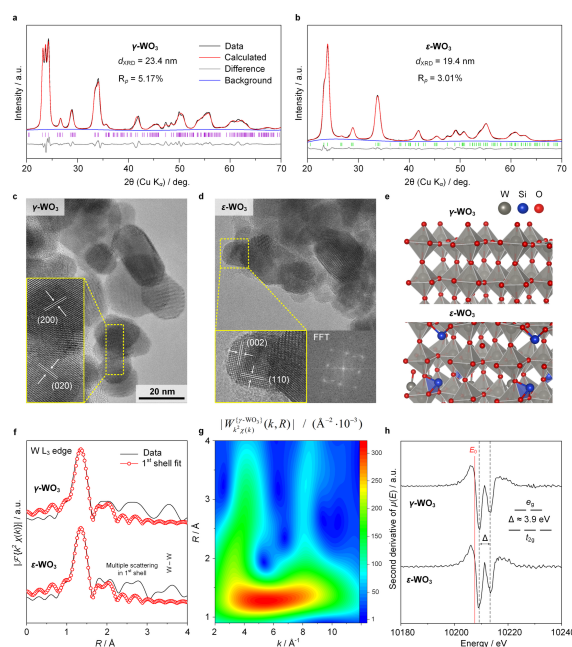


Fig. 1. Structural and spectroscopic characterization of γ -WO₃ and ϵ -WO₃: (a,b) XRD patterns and Rietveld refinements, (c,d) high-resolution TEM, (e) DFT-relaxed structures, (f) W-L₃-edge Fourier transforms, (g) wavelet transform magnitude for γ -WO₃, and (h) second derivative of XANES.

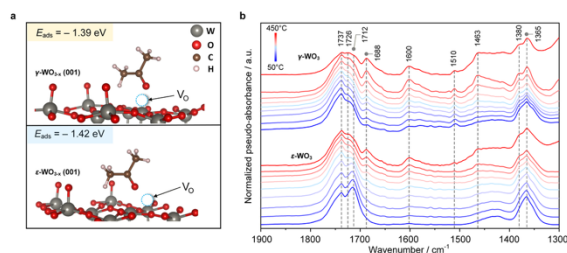


Fig 2. (a) Equilibrium structures of γ -WO_{3-x}(001) and ϵ -WO_{3-x}(001) with an adsorbed acetone molecule. Shown are the adsorption energies obtained by DFT. (b) In situ DRIFT spectra of adsorbed acetone (2 vol% C₃H₆O) between 50 – 450 °C in steps of 50 °C.

analyte induced changes were probed by in situ DRIFT spectroscopy, chemoresistive sensing and related experiments. In parallel, DFT calculations were carried out to determine the adsorption energy, charge transfer, differential charge density, and band structure upon acetone adsorption. This combined approach enabled us to correlate molecular interaction with polymorph-dependent electronic transduction in WO₃.

Results

Structural identity of WO₃ polymorphs

Using flame spray pyrolysis [2], we synthesized γ -WO₃ and Si-stabilized ϵ -WO₃ nanoparticles. As shown in Fig. 1, XRD and HR-TEM confirmed phase-pure γ - and ϵ -WO₃ with faceted nanocrystals. DFT suggests that Si is incorporated interstitially, forming distorted SiO_x units that locally strain and stabilize the metastable ϵ -phase. W-L₃-edge XAFS shows similar W–O bond lengths and reduced coordination numbers in both polymorphs, indicating comparable local WO₆ environments with oxygen vacancies. Wavelet-transform analysis reveals additional Si-related distorted structures in ϵ -WO₃ beyond the first W coordination shell. Despite these differences, second-derivative XANES indicates nearly identical W⁶⁺ oxidation states and ligand-field splitting, showing that Si stabilizes ϵ -WO₃ without significantly perturbing the local WO₆ framework.

Acetone adsorption and surface chemistry

To clarify analyte–surface interactions, we combined DFT calculations within in situ DRIFT spectroscopy. DFT-relaxed structures show that acetone preferentially adsorbs via its carbonyl oxygen on under-coordinated W sites *next* to oxygen vacancies in both γ - and ϵ -WO_{3-x} (Fig. 2a). The calculated adsorption energies are nearly identical (–1.39 eV for γ -WO_{3-x} and –1.42 eV for ϵ -WO_{3-x}), together with comparable charge transfer, indicating similar surface binding in the two polymorphs. In situ DRIFTS during acetone exposure further shows similar surface chemistry for γ - and ϵ -WO₃ (Fig. 2b). Acetone adsorption

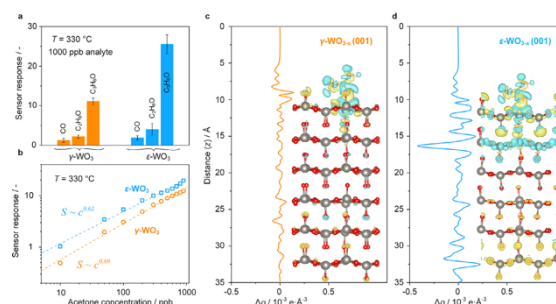


Fig. 3. (a) Sensor response of γ -WO₃ (orange) and ϵ -WO₃ (blue) toward 1000 ppb CO, ethanol, and acetone as well as (b) response vs. concentration characteristics of these for acetone ranging between 10 and 1000 ppb. CDD maps as well as plane-averaged differential density ($\Delta\rho$) plot as a function of z-coordinate (i.e., normal to the slab) of acetone adsorbed on (001) surfaces of (c) γ -WO_{3-x} and (d) ϵ -WO_{3-x}.

gives perturbed C=O bands, indicating interaction with surface W sites, while a weaker low-wavenumber component suggests more strongly activated species. Importantly, within the typical sensing range of 300–400 °C, both polymorphs exhibit nearly identical surface reactivity, indicating that their response difference does not primarily arise from receptor chemistry.

Transducer function and electronic structure

Despite similar acetone adsorption and surface chemistry, ϵ -WO₃ shows higher chemoresistive responses than γ -WO₃, indicating that the performance difference arises from transduction rather than receptor chemistry. As shown in Fig. 3a, this polymorph-dependent response is most pronounced for acetone compared with CO and ethanol. DFT-calculated charge-density-difference (CDD) analysis reveals pronounced subsurface charge redistribution only in ϵ -WO₃ after acetone adsorption (Fig. 3c, d). This behavior can be understood from the electronic structure. In contrast to γ -WO₃, ϵ -WO₃ more readily accommodates analyte-induced electrons in conduction-relevant W(5d)-dominated states close to the conduction-band edge, thereby providing an efficient pathway for conductivity modulation. Together with the orbital-resolved analysis and local W–O distortions, these results suggest the formation of delocalized electron polarons across several subsurface W atoms. Thus, polymorphism in WO₃ governs chemoresistive sensing behavior mainly by tuning the density and accessibility of conduction-relevant states.

References

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