

Non-Equilibrium Near-Surface Reconstruction Enhances Chemical-to-Electrical Transduction in Metal Oxide Sensors

Jia Huang

huangjia@tongji.edu.cn

Tongji University <https://orcid.org/0000-0002-2873-7704>

Yongwei Li

Tongji University

Changchun Ye

Guangdong University of Technology

Haomeng Qiu

Tongji University

Chenshuang Pan

Tongji University

Jie Yang

Tongji University <https://orcid.org/0000-0002-1472-198X>

Article

Keywords: non-equilibrium near-surface reconstruction, chemical-to-electrical transduction, thermochemical quenching, metal oxide gas sensors, intelligent sensing

Posted Date: October 27th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11232623/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: There is **NO** Competing Interest.

Non-Equilibrium Near-Surface Reconstruction Enhances Chemical-to-Electrical Transduction in Metal Oxide Sensors

Yongwei Li,^{†, [a]} Changchun Ye,^{†, [b]} Haomeng Qiu,^[a] Chenshuang Pan,^[a] Jie Yang,^{*, [a]} Jia Huang,^{*, [a]}

Yongwei Li and Changchun Ye contributed equally to this work.

^[a] School of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China

E-mail: yangji@tongji.edu.cn (J. Yang); huangjia@tongji.edu.cn (J. Huang)

^[b] School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, P. R. China

Abstract

Gas sensors based on metal oxides are conventionally optimized by maximizing surface reactivity, yet stronger surface chemistry does not guarantee a proportionally larger electrical signal, because localized chemical events must be efficiently transmitted into the charge-transport pathway. Herein, we introduce non-equilibrium near-surface reconstruction as a general materials design principle that strengthens this chemical-to-electrical transduction. Thermochemical quenching kinetically stabilizes a metastable near-surface state in WO_3 that combines oxygen vacancies, lattice distortions, and highly dispersed Ni species with reconfigured local coordination, while largely preserving the bulk crystal structure. Spectroscopic analysis, in situ infrared measurements, and density functional theory calculations reveal that this non-equilibrium state simultaneously accelerates NO_2 adsorption and surface-reaction kinetics and funnels adsorption-induced charge redistribution into transport-relevant electronic states. The optimized sensor delivers a response of 21.3 toward 1 ppm NO_2 at 150 °C, a response time of 3.5 s, and a theoretical detection limit of 52 ppt. The concept is further extended to multiple metal oxides, and an integrated array of the reconstructed oxides discriminates six gases with 96.25% classification accuracy assisted by a convolutional neural network. These results identify non-equilibrium near-surface reconstruction as a general route to improve chemical-to-electrical transduction by coupling surface reactivity with electronic transport, rather than optimizing surface chemistry alone.

Keywords: non-equilibrium near-surface reconstruction, chemical-to-electrical transduction, thermochemical quenching, metal oxide gas sensors, intelligent sensing

Introduction

Metal-oxide semiconductor (MOS) sensors transduce molecular interactions at solid surfaces into electrical signals, providing a widely accessible platform for chemical detection in environmental monitoring, industrial safety, and health-related applications^[1-5]. Considerable progress has been achieved by tailoring surface chemistry through noble-metal functionalization^[6, 7], defect engineering^[8, 9], heterostructure construction^[10, 11], and related materials strategies^[12, 13]. These approaches can substantially promote molecular adsorption and activation; however, enhanced surface reactivity does not necessarily translate into a proportional electrical response^[14, 15]. This distinction arises because chemiresistive sensing is not solely a surface-reaction process, but a multiscale transduction process in which localized adsorption or reaction events must induce charge redistribution, perturb the carrier depletion or accumulation region, and ultimately modulate an extended conductive pathway^[16-18]. Consequently, even highly reactive surface configurations may produce only modest resistance changes when the associated electronic perturbation is inefficiently transmitted to charge transport. Efficient conversion of localized chemical events into macroscopic electrical signals therefore represents an important and comparatively underexplored bottleneck in MOS sensing.

The near-surface region is particularly important to this chemical-to-electrical transduction because it simultaneously hosts molecular interactions and mediates their influence on carrier transport. In materials prepared under equilibrium or near-equilibrium conditions^[19-21], high-energy lattice distortions^[22], metastable defects^[23], and locally perturbed coordination environments^[24] tend to relax toward thermodynamically favored configurations. As a result, chemically reactive configurations and transport-responsive electronic states can become only weakly coupled, limiting the extent to which adsorption-induced charge redistribution perturbs the conductive pathway. Overcoming

this limitation therefore requires more than simply increasing the density of adsorption sites or defects. Instead, an effective sensing architecture should establish a near-surface state in which chemically active configurations coexist and strongly interact with electronic states relevant to charge transport, enabling a local chemical perturbation to generate a substantial modulation of carrier density and conductance. Such a metastable chemical-electronic state is intrinsically difficult to access through conventional equilibrium processing, suggesting that non-equilibrium materials engineering may provide a route to strengthening chemical-to-electrical transduction.

Quenching has recently emerged as a powerful route to metastable oxide surfaces: it has been exploited to functionalize near-surface metal atoms for electrocatalytic water oxidation^[25] and to drive structural transformations toward heterostructured oxides^[26]. These studies established that non-equilibrium near-surface states can be deliberately created and stabilized. In gas sensing, however, the central unresolved question is not how to make surfaces more reactive, but how to convert surface chemistry into electrical signals more efficiently. Whether such non-equilibrium near-surface states can be harnessed to strengthen this chemical-to-electrical transduction, the defining step of chemiresistive sensing, has remained unexplored.

Here, we employ thermochemical quenching as a non-equilibrium route to kinetically stabilize such a metastable near-surface state in metal oxides. As a model system, high-temperature WO_3 nanoparticles are rapidly quenched in a low-temperature Ni-containing salt solution, suppressing near-surface structural relaxation while preserving the bulk monoclinic framework. The resulting reconstructed region combines lattice distortions, oxygen vacancies, and highly dispersed Ni species with reconfigured local coordination. Rather than functioning simply as additional adsorption sites, these coupled structural and electronic perturbations reshape both the surface reaction environment and its communication with charge transport. Spectroscopic characterization,

in situ infrared measurements, and density functional theory calculations show that the reconstructed state simultaneously promotes NO₂ adsorption and reaction kinetics and enhances adsorption-induced charge redistribution into transport-relevant electronic states. This strengthened chemical-electrical coupling leads to a response of 21.3 toward 1 ppm NO₂ at 150 °C, a response time of 3.5 s, and a theoretical detection limit of 52 ppt. The non-equilibrium reconstruction concept is further extended to multiple metal oxides and incorporated into a multi-gas sensing array. These results establish non-equilibrium near-surface reconstruction as a materials design framework for enhancing chemical-to-electrical transduction by coupling surface chemistry with electronic transport, rather than optimizing surface reactivity alone.

Results and Discussion

Synthesis and surface property

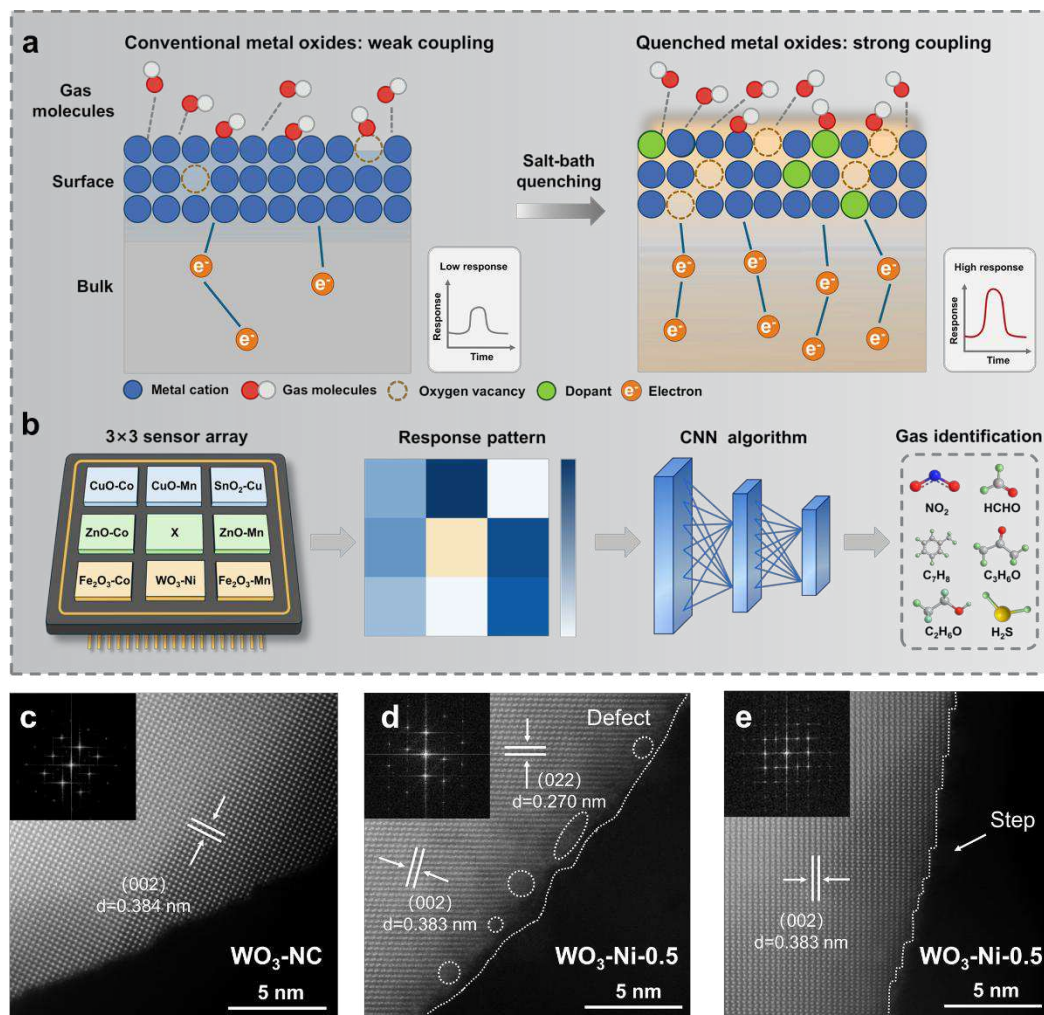


Figure 1. Design concept and structural evidence of non-equilibrium near-surface reconstruction for enhanced chemical-electrical transduction. **(a)** Schematic comparison of conventional metal oxides and quenched metal oxides. **(b)** Schematic diagram of the CNN model for feature extraction and pattern analysis to discriminate six distinct gas species. Aberration-corrected scanning transmission electron microscopy (AC-STEM) images of **(c)** WO₃-NC and **(d-e)** WO₃-Ni-0.5, along with the corresponding FFT patterns.

Efficient chemical-electrical transduction in metal-oxide gas sensors relies on the direct coupling between surface reactions and charge transport. However, in conventional equilibrium-processed metal oxides, these two processes are spatially separated. Surface reactions occur at localized sites, whereas charge transport is governed by the near-surface or bulk region. This

spatial mismatch significantly attenuates the impact of local chemical perturbations on the conductive pathway. Therefore, an effective sensing architecture should co-localize chemically active sites with electronically responsive states within the near-surface region.

To realize such a co-localized near-surface state, we employed a non-equilibrium salt-bath quenching process to reconstruct the near-surface structure of WO_3 -based gas-sensitive materials. As illustrated in **Figure S1**, high-temperature WO_3 nanoparticles were rapidly quenched in 0 °C metal salt solutions, generating a thermochemical shock that suppresses near-surface relaxation and kinetically stabilizes metastable configurations. This process enables the formation of a reconstructed near-surface region containing lattice distortions, oxygen vacancies, and incorporated metal species^[27]. Compared with conventional metal oxides with weak chemical-electrical coupling, the quenched surface is expected to co-localize chemically active sites and transport-relevant electronic states, thereby amplifying gas-induced charge redistribution into a measurable resistance response (**Figure 1a**). WO_3 samples quenched in $\text{Ni}(\text{NO}_3)_2$ aqueous solutions were denoted as $\text{WO}_3\text{-Ni-X}$, where X represents the $\text{Ni}(\text{NO}_3)_2$ concentration of 0.1, 0.5, or 1.0 M. For comparison, WO_3 samples quenched in 0.5 M $\text{Fe}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$ solutions were labeled as $\text{WO}_3\text{-Fe}$ and $\text{WO}_3\text{-Co}$, respectively. Beyond single-material optimization, this non-equilibrium strategy was further extended to different metal oxides and integrated into a sensor array (**Figure 1b**). Because each reconstructed oxide possesses distinct surface chemistry and electronic response characteristics, different gases generate unique response patterns across the array. These multidimensional patterns can then be processed by a convolutional neural network for gas identification, linking surface-level transduction enhancement with array-level intelligent sensing.

The phase structure and morphology of the representative samples were examined. X-ray diffraction (XRD) patterns confirm that both the naturally

cooled ($\text{WO}_3\text{-NC}$) and quenched $\text{WO}_3\text{-Ni-0.5}$ samples exhibit monoclinic characteristic peaks of WO_3 (JCPDS No. 83-0951), with no additional diffraction peaks associated with Ni species after quenching (**Figure S2**). Meanwhile, scanning electron microscopy (SEM) images (**Figure S3**) show that both $\text{WO}_3\text{-NC}$ and $\text{WO}_3\text{-Ni-0.5}$ are spherical nanoparticles with an average size of approximately 70 nm, suggesting that the quenching treatment does not significantly alter the overall morphology of WO_3 , with the induced modifications likely confined to the near-surface region. The atomic-scale influence of the quenching process is further revealed by aberration-corrected scanning transmission electron microscopy (AC-STEM). The naturally cooled $\text{WO}_3\text{-NC}$ exhibits a smooth, defect-free surface with a complete lattice structure (Figure 1c). In contrast, $\text{WO}_3\text{-Ni-0.5}$ exhibits irregular surface edges and abundant defects, such as step edges and lattice distortions (**Figure 1d-e**). These characteristics can be attributed to the synergistic effects of rapid thermal quenching and cationic doping, which perturb the surface lattice and stabilize high-energy configurations in the near-surface region^[25, 26]. The presence of surface defects and step-edge structures enhances local chemical reactivity and promotes charge redistribution upon gas interaction, which is essential for coupling surface reactions to electronic transport^[25]. This behavior is consistent with our design principle of constructing a cooperative near-surface architecture that simultaneously supports chemical perturbations and charge carrier modulation. Energy-dispersive X-ray spectroscopy (EDX) shows no Ni-rich domains or elemental segregation, ruling out compositional inhomogeneity as the origin of the surface defects. The defects thus arise from quenching-induced lattice perturbation synergized with Ni incorporation (**Figure S4**).

Structural transformation induced by quenching

X-ray photoelectron spectroscopy (XPS) was employed to analyze the elemental composition and chemical states of $\text{WO}_3\text{-Ni-0.5}$ and $\text{WO}_3\text{-NC}$. The

full-scan spectra of both materials confirm the presence of W and O elements (**Figure S5**) and additionally reveal Ni signals in WO₃-Ni-0.5. High-resolution Ni 2p spectra of WO₃-Ni-0.5 show four main peaks at 853.7 eV, 870.8 eV, 856.3 eV, and 874.8 eV (**Figure 2a**), which are characteristic of Ni²⁺ and Ni³⁺ species^[28, 29]. The coexistence of doped Ni in the form of Ni³⁺ and Ni²⁺ suggests that the quenching process induces partial oxidation of Ni²⁺, and the Ni²⁺/Ni³⁺ redox couple is expected to facilitate NO₂ adsorption and activation through redox-mediated surface reactions^[30]. High-resolution W 4f spectra (**Figure 2b**) show that both WO₃-NC and WO₃-Ni-0.5 are dominated by W⁶⁺, with a small amount of W⁵⁺. A slight positive shift of the W 4f peaks in WO₃-Ni-0.5 relative to WO₃-NC suggests a modified local electronic environment and a reconfigured electronic density around W sites^[31, 32]. Electron paramagnetic resonance (EPR) spectra of WO₃-Ni-0.5 and WO₃-NC both reveal a signal at g = 2.003, a signature of unpaired electrons associated with oxygen vacancies (**Figure 2c**). The enhanced intensity of this signal in WO₃-Ni-0.5 confirms that the quenching treatment generates a higher concentration of oxygen vacancies. Further quantitative analysis shows that the oxygen-vacancy concentration in WO₃-Ni-0.5 is 42.9% higher than that in WO₃-NC (**Figure S6**), confirming that the thermochemical shock effectively locks a high density of defects within the lattice, which is also confirmed by the O 1s spectra (**Figure S7**). The O 1s spectra display three distinct peaks at 530.1 eV, 530.7 eV, and 531.9 eV, corresponding to lattice oxygen (O_L), oxygen vacancies (O_V), and chemisorbed oxygen (O_C), respectively. The pronounced shift of the oxygen peak in WO₃-Ni-0.5 toward higher binding energy stems from a higher concentration of oxygen vacancies, providing more chemically active sites for NO₂ interactions^[32]. These XPS results are consistent with the designed non-equilibrium near-surface reconstruction and support the formation of a chemically responsive near-surface region. Raman spectra reveal no discernible shift in the characteristic peaks after quenching, indicating that the long-range crystal structure remains

largely preserved (**Figure 2d**). In contrast, the reduced peak intensity suggests increased local disorder in the near-surface region (**Figure S8a**). This trend is consistent with the enhanced near-surface structural disorder and increased oxygen-vacancy density revealed by XPS and EPR analyses. Similar intensity reduction is observed for WO₃-Fe and WO₃-Co (**Figure S8b**), further supporting that quenching in different metal nitrate solutions induces comparable defect-rich surface states.

To gain deeper insight into the local coordination environment and oxidation states, X-ray absorption spectroscopy (XAS) was conducted. Ni K-edge X-ray absorption near-edge structure (XANES) spectra (**Figure 2e**) show that the Ni absorption edge of WO₃-Ni-0.5 is shifted to higher energy and exhibits a more intense white-line feature compared with NiO, indicative of partially oxidized Ni species^[33]. This observation is consistent with the coexistence of Ni²⁺ and Ni³⁺ revealed by XPS. Concurrently, the W L₃-absorption edge in WO₃-Ni-0.5 exhibits an enhanced white-line peak relative to WO₃-NC (**Figure S9a**), further supporting the modified electronic structure of W, in agreement with the W 4f binding-energy shift^[34]. Ni K-edge extended X-ray absorption fine structure (EXAFS) analysis (**Figure 2f**) shows a distinct Ni-O peak in WO₃-Ni-0.5 and the absence of the Ni-Ni peak. These features indicate that Ni interacts chemically with the oxygen framework of WO₃ and that Ni species are highly dispersed. W L₃-edge EXAFS (**Figure S9b**) shows a slight reduction in the intensity of the W-O peak in WO₃-Ni-0.5, which may reflect increased surface disorder or defect density around W sites, consistent with the presence of oxygen vacancies and near-surface reconstruction^[35]. The 3D wavelet transform (WT) plots of WO₃-Ni-0.5 (**Figure 2g, h**) provide unambiguous spatial resolution of the scattering contributions. The simultaneous emergence of intense signals from both Ni-O and W-O coordination shells confirms that the non-equilibrium reconstruction entails a collective rearrangement of local environments rather than isolated single-site

doping. This cooperative Ni-O/W-O configuration thus serves as the primary structural evidence for a synergistic near-surface architecture, which is poised to facilitate the subsequent adsorption and activation of NO₂ molecules.

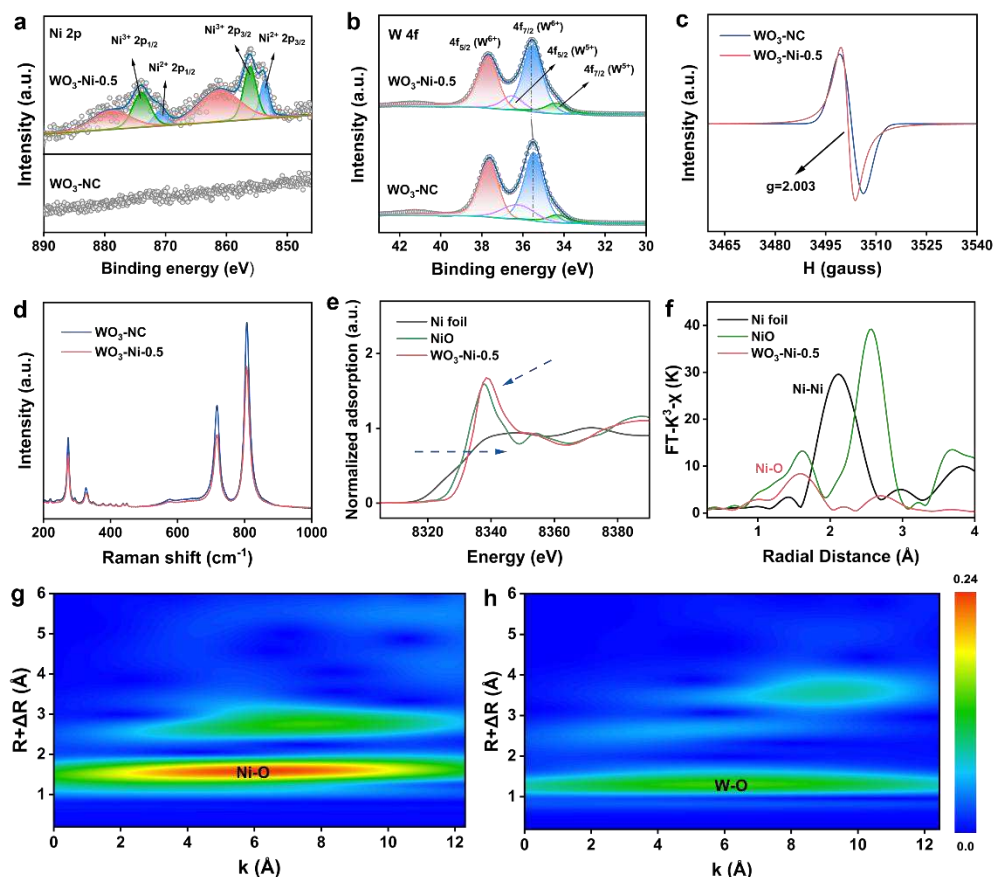


Figure 2. Reconfiguration of the near-surface electronic structure under non-equilibrium conditions. High-resolution XPS spectra of the as-prepared WO₃-Ni-0.5 and WO₃-NC showing (a) Ni 2p and (b) W 4f, respectively. (c) Electron Paramagnetic Resonance (EPR) testing curves for WO₃-Ni-0.5 and WO₃-NC. (d) Raman spectra of WO₃-Ni-0.5 and WO₃-NC. (e) Normalized XANES spectra of the Ni K-edge. (f) Fourier-transformed k³χ(R) Ni K-edge EXAFS for WO₃-Ni-0.5. 3D wavelet transforms diagrams for (g) Ni and (h) W, respectively.

Collectively, the above characterization results indicate that the quenching treatment effectively reconstructs the near-surface region of WO₃ nanoparticles while preserving their bulk crystal structure. This leads to the stable coexistence of highly dispersed Ni species and abundant oxygen vacancies, which modifies the local electronic structure and surface charge distribution. Consequently, the

engineered surface in WO₃-Ni-0.5 promotes interfacial charge transfer and enhances the coupling between NO₂ adsorption/activation and the conductance response of the sensing layer.

Gas-sensing performance

The sensing performance directly reflects the effectiveness of chemical-electrical transduction. The gas-sensing behavior of WO₃-Ni-0.5 was investigated using a ceramic-tube-based sensor platform (**Figure S10**). WO₃ is a typical n-type semiconductor in which electrons act as the majority charge carriers. In air, oxygen molecules adsorb on the WO₃ surface and extract electrons from the conduction band, forming activated O_x⁻ species and generating an electron depletion layer near the surface (**Figure 3a**). This depletion layer leads to a relatively high baseline resistance. Upon exposure to NO₂, a strong oxidizing gas, NO₂ further captures electrons from the conduction band to form adsorbed NO₂⁻ species, which significantly enlarges the depletion region and results in a pronounced increase in resistance. This behavior provides a direct link between the near-surface electronic structure and the macroscopic conductance response.

The response (S) is defined as $S = R_g/R_a$ for oxidizing gases (for reducing gases, $S = R_a/R_g$), where R_g and R_a represent the sensor resistances in the target gas and in air, respectively. The results of gas sensing at room temperature (**Figure 3b**) reveal that all materials respond robustly to 1 ppm NO₂, and WO₃-Ni-0.5 shows the highest performance, achieving a response of 5.1. This demonstrates that WO₃-Ni-0.5 exhibits a markedly enhanced response compared with pristine WO₃. At lower Ni concentrations (0.1 M), the defect density and electronic modulation are insufficient to significantly enhance the sensing performance. At higher Ni concentrations (1.0 M), excessive dopant-induced defects and impurities introduce additional trapping and scattering centers, which reduce carrier mobility and slow the response and

recovery processes^[36]. The peak response at 0.5 M reflects a critical balance between increased chemical activity and efficient charge transport, enabling the most effective coupling between surface reactions and electrical modulation. The response of WO₃-Ni-0.5 to NO₂ increases proportionally with concentration in the 0.1-1 ppm range at room temperature and follows a linear relationship (**Figure 3c**). Notably, the theoretical LOD of the sensor at room temperature is estimated to be 1.71 ppb (**Figure S11**). These results demonstrate that the high-energy surface configurations created by quenching bypass the thermal activation barriers typically required for traditional WO₃-based sensors, enabling highly sensitive NO₂ detection at room temperature.

To optimize the working temperature, the sensing response of WO₃-Ni-0.5 to 500 ppb NO₂ was measured from 50 °C to 200 °C (**Figure S12**). The response initially rises and then decreases with increasing temperature, reaching a maximum at 150 °C. The performance decline at higher temperatures is attributed to enhanced lattice vibrations (phonons), which increase the frequency of electron-phonon scattering during electron transport and reduce electron mobility, thereby degrading the sensing response^[37]. Consequently, 150 °C was selected as the optimal working temperature for subsequent tests.

To further optimize material performance, WO₃ samples quenched in solutions of different transition metals (Fe, Co, Ni) were prepared, and their sensing responses to 1 ppm NO₂ were evaluated (**Figure S13**). The WO₃-Ni-0.5 sensor exhibits the highest response of 21.3, approximately 5.0-fold higher than that of WO₃-NC. In contrast, WO₃-Fe shows a lower response, possibly due to the formation of electron trap states that impede effective charge transfer during sensing. WO₃-Co exhibits only a slight change compared with WO₃-NC, indicating that Co doping has a limited impact on the electronic structure and surface reactivity under the present conditions. Further investigations were carried out on the sensing performance of WO₃ quenched in Ni salt solutions

of varying concentrations (0.1, 0.5, and 1.0 M) at 150 °C (**Figure 3d**). The response trend remains consistent with that observed at room temperature.

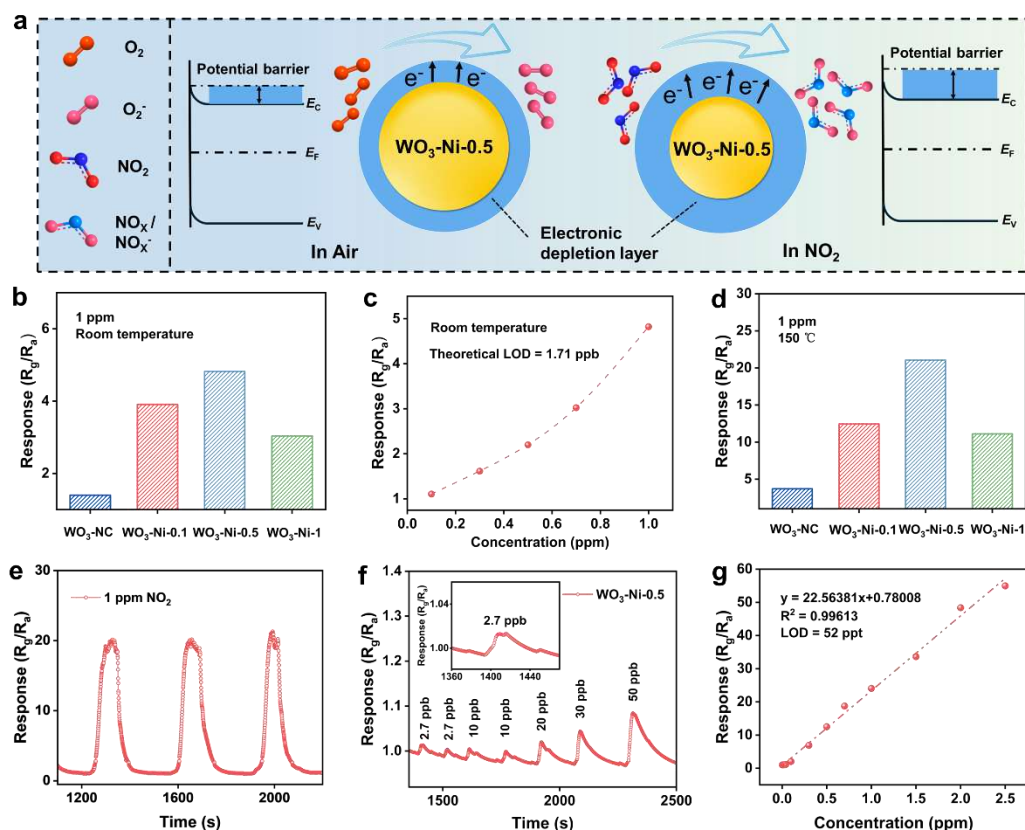


Figure 3. Enhanced NO₂ transduction performance enabled by the reconstructed near-surface architecture. **(a)** Schematic diagram of the NO₂ sensing mechanism on WO₃. **(b)** Response of different sensors to 1 ppm NO₂ at room temperature. **(c)** Response of WO₃-Ni-0.5 sensor versus different NO₂ concentrations (0.1-1 ppm) at room temperature. **(d)** Response of different sensors to 1 ppm NO₂ at 150 °C. **(e)** Repeated response-recovery cycles of the WO₃-Ni-0.5 sensor to 1 ppm NO₂ at 150 °C. **(f)** Dynamic response-recovery curve of WO₃-Ni-0.5 sensor at different ppb-level concentrations (2.7 ppb-50 ppb). **(g)** Linearity of WO₃-Ni-0.5 sensor from 0.0027 to 2.5 ppm NO₂ at 150 °C.

In addition, the WO₃-Ni-0.5 sensor exhibits excellent cyclic stability. As shown in **Figure 3e**, the response-recovery cycles during repeated exposure to 1 ppm NO₂ remain nearly identical, indicating remarkable sensor stability. Similar cyclic behaviors are also observed for the other materials (**Figures S14 and S15**), demonstrating good repeatability. The WO₃-Ni-0.5 sensor shows stable and reversible sensing behavior across varying NO₂ concentrations (**Figure S16**) due to its abundant active sites and enhanced electron transport.

Its resistance increases with rising NO₂ concentration and returns nearly to the baseline after gas removal. The response value (defined as $S = R_g/R_a$) increases from 2.03 to 55.82 as NO₂ concentration rises, indicating a pronounced concentration dependence. This enhanced response originates from the reconstructed near-surface region, where the co-localization of active sites and electronic states lowers NO₂ adsorption barriers and improves charge transfer, collectively enabling efficient charge transduction. Similar concentration-dependent curves for other materials are shown in **Figures S17 and S18**, with the response values increasing proportionally to the NO₂ concentration. Moreover, the non-equilibrium quenching strategy engineers the material's surface and electronic structure, enabling the coupling of chemical and electronic states, which efficiently translates subtle chemical perturbations into measurable electrical responses. As shown in **Figures 3f and S19**, the WO₃-Ni-0.5 sensor can detect NO₂ concentrations as low as 2.7 ppb. Notably, the sensor demonstrates an exceptionally low theoretical LOD of 52 ppt (**Figure 3g**), calculated based on threefold noise level and the linear correlation between the resistance response and NO₂ concentration. This extremely low detection limit demonstrates that the non-equilibrium quenching effectively converts minute surface chemical fluctuations into strong, detectable electrical signals. These results confirm that non-equilibrium near-surface engineering effectively overcomes the intrinsic transduction bottleneck in conventional systems.

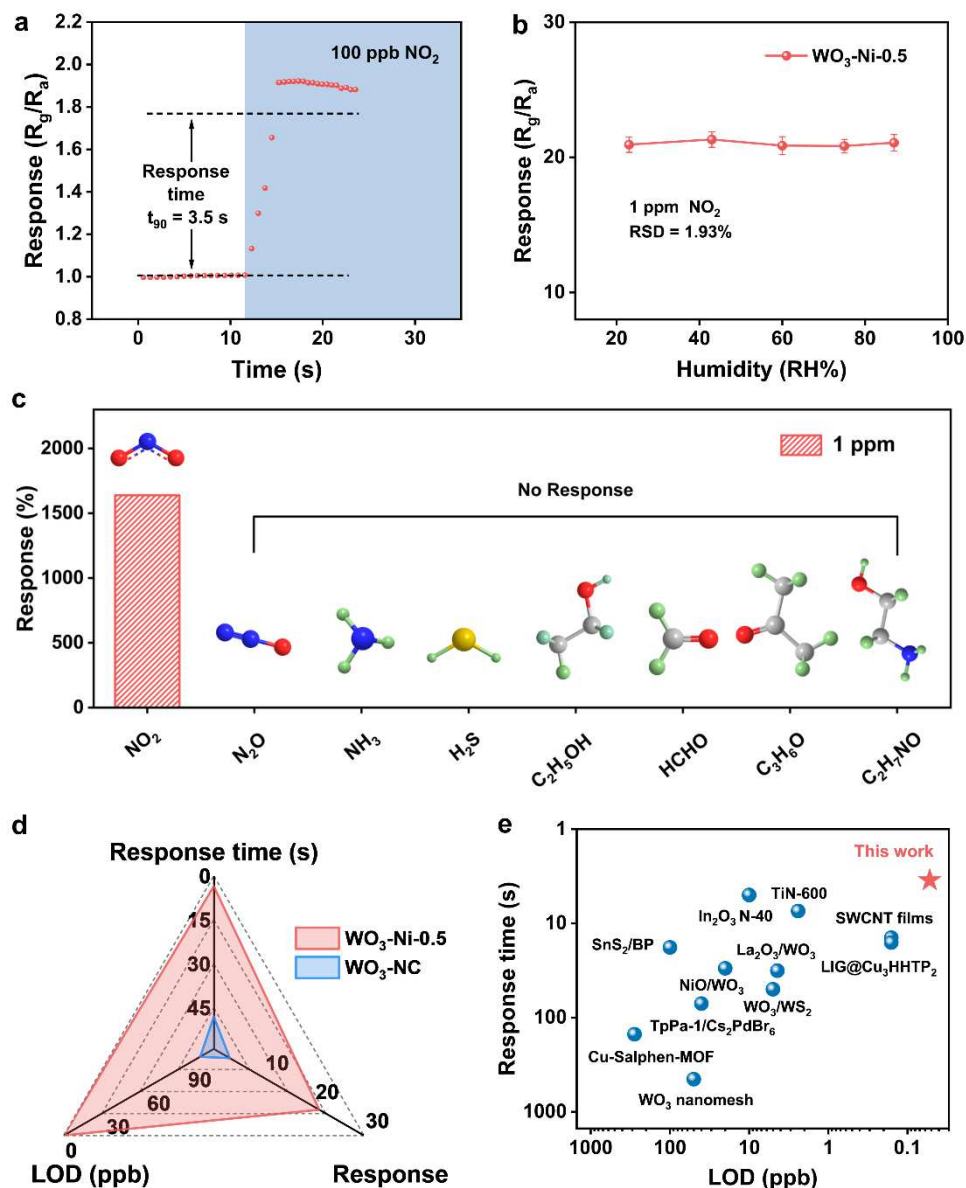


Figure 4. Practical NO_2 sensing characteristics of $\text{WO}_3\text{-Ni-0.5}$. **(a)** Response time of $\text{WO}_3\text{-Ni-0.5}$ sensor to 100 ppb NO_2 . **(b)** Response variation under different humidity levels. **(c)** Selectivity toward NO_2 over other interfering gases (1 ppm). **(d)** Radar chart comparison of $\text{WO}_3\text{-Ni-0.5}$ (red) and $\text{WO}_3\text{-NC}$ (blue) sensors. **(e)** Comparison with other NO_2 sensing materials in terms of LOD and response time.

Beyond the response magnitude at trace concentrations, the rate at which these surface chemical events are transduced into electrical signals is equally critical for practical sensing. The $\text{WO}_3\text{-Ni-0.5}$ sensor exhibits a rapid response time of 3.5 s to 100 ppb NO_2 (**Figure 4a**), which is shorter than the 48 s required by $\text{WO}_3\text{-NC}$ (**Figure S20**). This accelerated response is attributed to the

electronically reconfigured near-surface region stabilized by the quenching strategy, which lowers the activation barrier for charge-carrier transfer at the gas-solid interface. This mechanism is further supported by subsequent theoretical calculations.

Additionally, ambient humidity is a critical factor influencing the performance of gas sensors. The response of the WO₃-Ni-0.5 sensor to 1 ppm NO₂ was systematically tested under varying relative humidity (RH) conditions ranging from 21 % to 87 % (**Figure 4b**). The sensor consistently exhibited a stable response value of approximately 21 across all RH levels, indicating exceptional moisture resistance. This stability is likely due to the quenching-induced modification of the WO₃ surface, which may be associated with suppressed competitive adsorption of H₂O on the modified surface^[36]. As a result, humidity has little effect on the sensor's performance. Furthermore, the anti-interference capability of the WO₃-Ni-0.5 sensor was systematically evaluated against common industrial and environmental interferents, including nitrous oxide (N₂O), ammonia (NH₃), hydrogen sulfide (H₂S), ethanol (C₂H₅OH), formaldehyde (HCHO), acetone (C₃H₆O), and ethanolamine (C₂H₇NO) (**Figure 4c**). At 1 ppm under identical conditions, the sensor shows a pronounced response to NO₂ while exhibiting negligible responses to other gases. In particular, N₂O and NH₃, which are often reported to interfere with NO₂ detection in similar sensors, did not cause noticeable signal changes, indicating high selectivity toward NO₂. This high selectivity is attributed to the high density of oxygen vacancies formed during quenching, which generate abundant electron-rich centers on the WO₃ surface^[38]. Such centers participate in electron donor-acceptor interactions with NO₂ molecules, driving targeted surface catalytic processes that lead to highly selective NO₂ sensing. Moreover, the WO₃-Ni-0.5 sensor maintains consistent performance with minimal signal drift over 180 days (**Figure S21**), further underscoring its excellent long-term durability and reliability.

To provide an integrated performance assessment, a radar chart (Figure 4d) compares WO₃-Ni-0.5 and WO₃-NC across key performance metrics, including response magnitude, response time, and LOD. The results demonstrate clear performance enhancements enabled by the quenching-engineered surface. In comparison with state-of-the-art NO₂ sensing materials (e.g., TMDs, metal oxides, organic-inorganic hybrids) reported in the literature, the WO₃-Ni-0.5 sensor demonstrates the shortest response time and the lowest LOD among the reported chemiresistive NO₂ sensors compiled in Table S1 (Figure 4e). These results highlight non-equilibrium near-surface reconstruction as an effective route to strengthening chemical-to-electrical transduction in high-performance gas-sensing platforms.

In situ FTIR analyses and DFT calculations

To elucidate the origin of the enhanced sensing performance, we combined in situ FTIR measurements with density functional theory calculations. FTIR analysis reveals the formation of reactive intermediates during NO₂ adsorption, indicating active surface chemistry at the reconstructed near-surface region. FTIR spectra show three distinct peaks at 1630, 2070, and 2251 cm⁻¹, corresponding to nitrate species, NO, and nitrite intermediates, respectively. Notably, the intensity of these peaks increases significantly upon exposure to NO₂ compared to the initial state, indicating the formation of reactive intermediates that can readily form even at room temperature, thereby facilitating electron exchange and enabling NO₂-related reactions under ambient conditions (**Figure 5a, b**). In situ FTIR spectra for the different samples are provided in **Figure S22**. WO₃-Ni-0.5 yields these intermediates faster than the other samples. This indicates that defects and dopants generated during quenching accelerate the surface reactions. To further elucidate the enhanced sensing mechanism of quenched WO₃, density functional theory (DFT) calculations were carried out. The structural models of WO₃-NC and WO₃-Ni-

0.5 are shown in **Figure 5c, d**, respectively. The vacancy defects on the WO₃-Ni-0.5 surface are consistent with those observed in the AC-STEM images (**Figure 1d, e**). The projected density of states (PDOS) plots (**Figure 5e, f**) reveal that quenching together with Ni doping causes strong orbital hybridization near the Fermi level, increasing the electron density in this region. The resulting shift of the Fermi level toward the conduction band increases the carrier concentration and facilitates more efficient electron participation in surface redox processes, thereby improving the sensing response^[39]. Furthermore, the d-band center of WO₃-Ni-0.5 is located at -3.218 eV, closer to the Fermi level ($E_f = 0$ eV) than that of WO₃-NC (-4.047 eV). The upward shift of the d-band center reduces antibonding-state occupation upon adsorption^[40], thereby strengthening adsorption and facilitating charge transfer during sensing.

In addition, quenching reduces the bandgap of WO₃-Ni-0.5 compared with WO₃-NC, which promotes more efficient electron migration. Differential charge density analysis based on Bader charge calculations was conducted during NO₂ adsorption on WO₃-NC and WO₃-Ni-0.5 (**Figure 5g**). The charge transfer between WO₃-Ni-0.5 and NO₂ reached 0.32 |e|, significantly higher than the 0.18 |e| observed for WO₃-NC. This enhanced charge transfer indicates that quenching improves the surface reactivity of WO₃-Ni-0.5, enabling more electrons to participate in NO₂ adsorption and activation, which contributes to an improved sensing response. Adsorption energy, which reflects the interaction strength between gas molecules and the material surface, was also evaluated. As shown in **Figures 5h** and **S23**, the adsorption energies of O₂ and NO₂ on the WO₃-Ni-0.5 surface are -0.4 eV and -1.34 eV, respectively, both of which are more negative than those on WO₃-NC (0.12 eV for O₂ and -0.78 eV for NO₂). These results demonstrate that quenching significantly enhances the adsorption capacity of WO₃-Ni-0.5 for NO₂, effectively lowers the activation energy of surface reactions, and accelerates the sensor response.

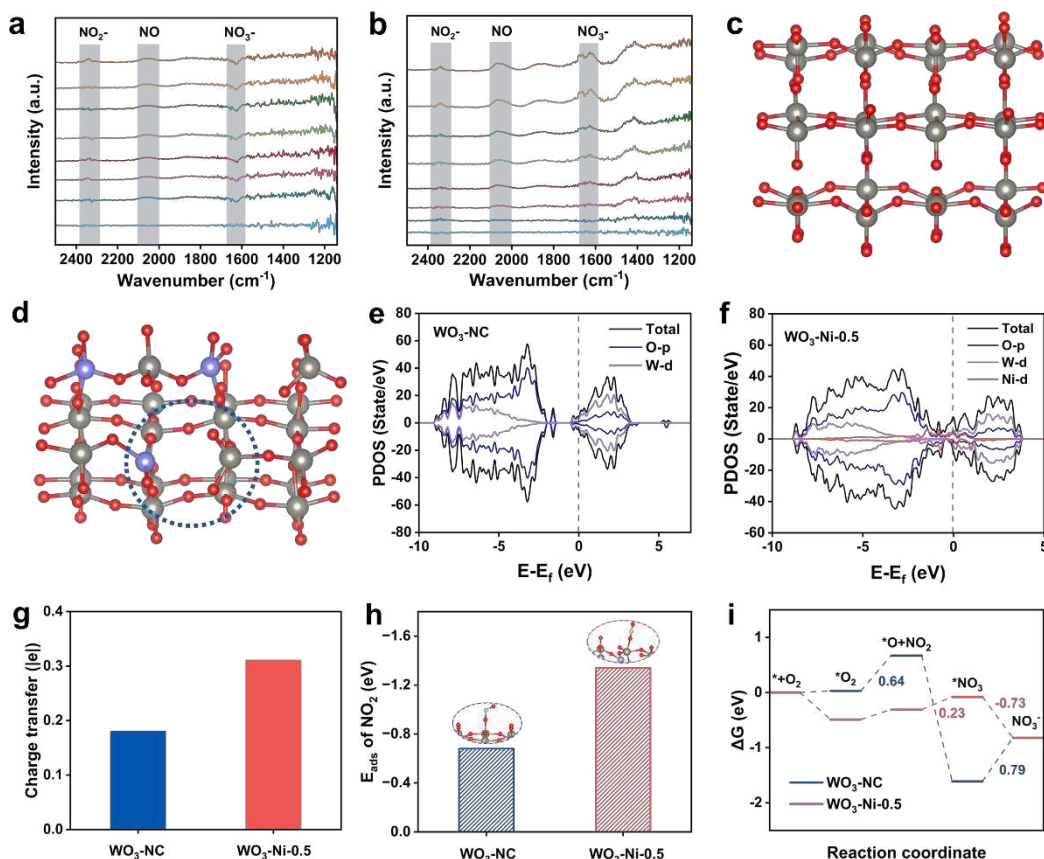


Figure 5. Surface reaction and electronic transduction mechanisms for NO₂ sensing. In situ FTIR spectra of NO₂ on the surface of WO₃-Ni-0.5 at various time intervals and temperatures: **(a)** 150 °C and **(b)** room temperature. **(c)** WO₃-NC structural model. **(d)** WO₃-Ni-0.5 structural model of defects, in which red, gray, and blue spheres represent oxygen, tungsten, and nickel atoms, respectively. The projected density of states (PDOS) calculated for **(e)** WO₃-NC and **(f)** WO₃-Ni-0.5. **(g)** The comparison of charge transfer between NO₂ and WO₃-NC or WO₃-Ni-0.5. **(h)** Comparison of adsorption energy of NO₂ between WO₃-NC and WO₃-Ni-0.5. **(i)** Comparison of the Gibbs free energy changes (ΔG) for the reaction of NO₂ on WO₃-Ni-0.5 and WO₃-NC.

To further elucidate the underlying mechanism of quenching and Ni doping on the NO₂ conversion process, we calculated the Gibbs free energy changes along the reaction pathway using DFT (**Figures 5i, S24, and S25**). Compared to WO₃-NC, WO₃-Ni-0.5 shows a significantly reduced free-energy barrier in the key reaction steps, indicating that its near-surface structure is more favorable for the formation and transformation of NO₂-related intermediates. Notably, in the process of generating the *NO₃ intermediate through the involvement of adsorbed oxygen, the reaction barrier for WO₃-Ni-0.5 is only 0.23 eV,

significantly lower than that of WO₃-NC (0.64 eV). This demonstrates that the non-equilibrium surface reconstruction effectively enhances the activation of reaction intermediates on the surface, thereby lowering the free-energy barrier of this key step. Moreover, during the desorption of the final nitrate product, WO₃-Ni-0.5 exhibits a significantly lower desorption free energy (-0.73 eV), while WO₃-NC still faces a substantial endothermic process (0.79 eV). The lower desorption energy barrier favors the rapid desorption of the product, thereby reducing the risk of active site passivation due to product coverage and promoting the continuous regeneration of active sites. These results indicate that the synergistic effect of Ni doping and non-equilibrium quenching-induced near-surface reconstruction not only lowers the energy barrier for the rate-determining step but also optimizes the product desorption process, enhancing reaction turnover efficiency and effectively suppressing response decay due to product accumulation during sensing. This, in turn, improves the stability and reliability of the device under long-term cyclic operation.

Based on the obtained experimental evidence, the surface reaction mechanism of WO₃-Ni-0.5 can be further elucidated. When the material is exposed to ambient air, oxygen molecules preferentially adsorb onto the WO₃-Ni-0.5 surface and capture electrons from the conduction band to form chemisorbed O₂⁻ species (**Equations 3 and 4**). This process induces the formation of an electron-depletion layer, corresponding to the high baseline resistance in the sensor signal. Upon exposure to NO₂, NO₂ molecules strongly adsorb at the defect-rich, Ni-coordinated surface sites and further capture electrons to form NO₂⁻ species (**Equation 5**). Simultaneously, NO₂ can participate in surface redox reactions with pre-adsorbed oxygen species (**Equation 6**). The synergistic effect of direct electron capture and oxygen-mediated surface reactions significantly enlarges the surface electron depletion region, leading to the pronounced change in electrical resistance observed in the experiments. It is noteworthy that NO was detected as a reaction product

during the process, providing direct experimental evidence that $\text{WO}_3\text{-Ni-0.5}$ participates in the partial decomposition of NO_2 at relatively low temperatures. This observation further supports a strong coupling between surface chemical events and charge-transport modulation, in which enhanced surface reactivity and efficient charge transfer are intrinsically linked.

Array-based electronic nose and multi-gas classification

With the continued evolution of the Internet of Things (IoT) and AI-driven environmental sensing systems toward intelligent and multi-scenario applications, the development of electronic nose platforms capable of identifying hazardous gases is of critical importance for industrial and public safety. In this work, multiple metal oxides regulated by a salt-bath quenching strategy were further integrated to construct an array-based electronic nose system. **Figure 6a** shows a top-view optical image of the device. The chip integrates a 3×3 sensor platform comprising eight sensing units and a central reference structure, in which the sensing units are spatially divided into distinct regions. Each region incorporates a different quenched metal oxide, including CuO-Co , CuO-Mn , $\text{SnO}_2\text{-Cu}$, ZnO-Co , ZnO-Mn , $\text{Fe}_2\text{O}_3\text{-Co}$, $\text{WO}_3\text{-Ni}$, and $\text{Fe}_2\text{O}_3\text{-Mn}$. A circular structure located at the center of the chip serves as a reference feature for device alignment and assembly. **Figure 6b** depicts the normalized spatial response patterns of the sensor array upon exposure to six target gases (formaldehyde, nitrogen dioxide, hydrogen sulfide, acetone, toluene, and ethanol). Owing to the distinct surface interactions between gas molecules and different metal oxides, the individual sensing units exhibit markedly different resistance variations. These heterogeneous responses give rise to distinct spatial patterns, which provide a physically meaningful feature basis for gas discrimination.

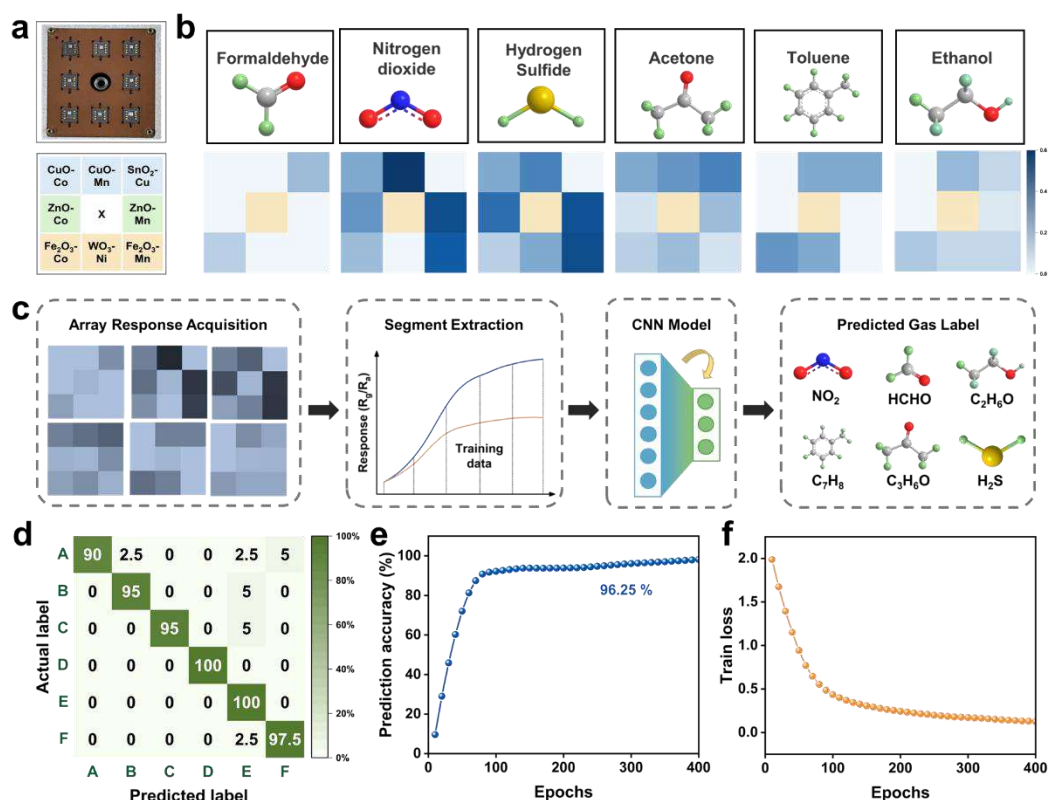


Figure 6. Bionic olfactory gas classification array based on quenched metal oxides. **(a)** Photograph and schematic illustration of the integrated metal oxide-based sensor array forming the electronic nose platform. **(b)** Normalized response patterns (greyscale from 0 to 0.6) of the sensor array to different gas species. **(c)** Workflow for dataset construction for gas classification. **(d)** Confusion matrix comparing the actual and predicted classes for six gases. (A, hydrogen sulfide; B, nitrogen dioxide; C, acetone; D, toluene; E, formaldehyde; F, ethanol). **(e)** Prediction accuracy versus training epochs for six-gas recognition. **(f)** Training loss versus epochs for gas species classification.

The processing framework for gas identification, utilizing the collective array response, is depicted in **Figure 6c**. Rather than relying on the response magnitude of individual sensors, this approach leverages the global spatiotemporal patterns generated by the entire array. The rising segments of the response curves are utilized to capture the dynamic adsorption kinetics of different gases. This materials-level heterogeneity is further decoded using a convolutional neural network (CNN) to map these high-dimensional spatiotemporal features onto discrete gas classes. The successful discrimination of the six target gases demonstrates the intrinsic pattern separability of the reconstructed metal oxide array, where different chemical

species form distinct, non-overlapping clusters in the feature domain. This confirms that the synergistic near-surface engineering provides a physically discriminative foundation for reliable multi-gas recognition. **Figure 6d** presents the confusion matrix obtained from CNN-based classification of the six gases, which is used to quantitatively evaluate the classification performance. The diagonal elements represent the proportion of correctly classified samples, whereas the off-diagonal elements correspond to misclassifications. Most samples are concentrated along the diagonal, indicating that the biomimetic olfactory array combined with the CNN can effectively discriminate among different gas species. The evolution of the prediction accuracy as a function of training epochs for the six-gas classification task is depicted in **Figure 6e**. As training proceeds, the prediction accuracy increases rapidly during the initial stage and then gradually saturates, eventually reaching a classification accuracy of 96.25%. Figure 6f shows the corresponding training loss as a function of training epochs for the same gas classification task. The loss decreases rapidly in the early stage of training and then gradually converges, indicating stable optimization behavior. These results suggest that the spatial response patterns obtained from the quenched metal oxide sensor array exhibit good learnability and can support stable and reliable gas classification performance. More importantly, the successful integration of diverse quenched MOS materials into a single functional array validates that the non-equilibrium near-surface engineering is broadly applicable and not limited to WO_3 . The system exhibits strong potential for operation in complex environments, offering a scalable sensing framework for embodied AI and advanced IoT applications.

Conclusion

This work addresses a fundamental limitation in metal-oxide gas sensing, demonstrating that effective sensing requires not only enhanced surface reactivity, but also efficient transmission of local chemical perturbations into

electronic transport. Thermochemical quenching provides a non-equilibrium route to kinetically stabilize a metastable near-surface state in WO_3 , where oxygen vacancies, lattice distortions, and highly dispersed Ni species with reconfigured local coordination coexist while the bulk crystal structure remains largely preserved. Spectroscopic, in situ, and theoretical analyses show that this reconstructed state simultaneously promotes NO_2 adsorption and surface-reaction kinetics and enhances adsorption-induced charge redistribution into transport-relevant electronic states. The resulting strengthening of chemical-electrical coupling gives rise to a response of 21.3 toward 1 ppm NO_2 at 150 °C, a response time of 3.5 s, and a theoretical detection limit of 52 ppt. Extension of the strategy to multiple metal oxides and an integrated multi-gas sensing array further supports its broader applicability. More broadly, these results establish non-equilibrium near-surface reconstruction as a materials design framework for enhancing chemical-to-electrical transduction by coupling surface chemistry with electronic transport, shifting sensor optimization from maximizing surface reactivity alone toward maximizing transduction efficiency.

Methods

Preparation of WO_3 nanoparticles

The pristine WO_3 nanoparticles were synthesized via a facile solvothermal method. Specifically, 1.0 g of WCl_6 was dissolved in 60 mL of anhydrous ethanol to form a clear solution. The solution was then transferred to a Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h. After natural cooling to room temperature, the solid product was collected by centrifugation, and washed three times with ethanol. The precursor was subsequently dried in a vacuum oven at 60 °C for 12 h. Finally, the dried precursor was calcined in a muffle furnace at 500 °C in air for 2 h and allowed to cool naturally to room temperature. The resulting product is denoted as $\text{WO}_3\text{-NC}$ (where NC denotes natural cooling).

Quenching of WO₃ nanoparticles

For the quenching experiments, WO₃ nanoparticles preheated to 500 °C in the muffle furnace were rapidly quenched in 0 °C Ni(NO₃)₂ solution with concentrations of 0.1, 0.5, and 1.0 M. The quenched samples were then collected by centrifugation, washed with deionized water, and dried at 60 °C for 12 h in the oven. The resulting products were labeled as WO₃-Ni-X, where X is the concentration of the metal salt in the quenching solution. Similarly, high-temperature WO₃ nanoparticles were rapidly quenched in 0.5 M solutions of Fe(NO₃)₃ and Co(NO₃)₂, and the corresponding products were labeled as WO₃-Fe and WO₃-Co, respectively. This rapid thermochemical quenching suppresses near-surface structural relaxation and kinetically stabilizes metastable near-surface configurations, while the bulk crystal structure and overall morphology are largely preserved.

Materials characterization

The structural and crystalline characteristics of the samples were investigated using X-ray powder diffraction (XRD, D8 ADVANCE). The morphology and size of the samples were observed using scanning electron microscopy (SEM, Zeiss Gemini 300). Aberration-corrected scanning transmission electron microscopy (AC-STEM) images were recorded on a Titan Cubed Themis G2 300. Surface elemental analysis was conducted via X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha), with binding energies calibrated against the C 1s peak (284.8 eV). X-ray absorption fine structure spectroscopy (XAFS) was carried out at the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF). Structural information was obtained through laser confocal Raman spectroscopy (LabRAM HR Evolution, excitation wavelength 532 nm). Oxygen vacancies were qualitatively and quantitatively analyzed by electron paramagnetic resonance (EPR, Bruker EMX Plus). In situ Fourier-transform infrared

spectroscopy (FTIR, Thermo IS 50) was employed to investigate the reaction intermediates, with all spectra recorded with an accumulation of 32 scans over the range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} .

Gas-sensing tests

The gas-sensing performance of all samples was evaluated using the SM1.1-C type gas-sensing measurement system. The fabrication procedure of the sensor involved the following steps: the sensing material powder synthesized by quenching was first dispersed in ethanol to form a homogeneous paste. The prepared paste was then deposited onto ceramic tubes and cured at 300 °C for 3 h. Each ceramic tube was coated with 3.0 ± 0.5 mg of the sensing material powder, resulting in an average coating thickness of approximately 500 μm .

The gas sensor array was fabricated via a custom MEMS process, mainly comprising an 8-sensor MOS array and embedded hardware running the gas classification algorithm. The selected sensing materials were individually deposited onto the array substrate and subjected to a controlled aging process. Optimal operating conditions were precisely maintained through the integrated microheater system.

The response time was defined as the time required for the resistance to rise from the baseline value to 90% of the maximum response upon exposure to the NO_2 gas. The theoretical limit of detection (LOD) was calculated from the Equation (1) recommended by IUPAC.

$$\text{LOD} = \frac{3 \times \text{rms}_{\text{noise}}}{S} \quad (1)$$

where S represents the slope of the linear fit line, and $\text{rms}_{\text{noise}}$ denotes the root mean square deviation.

DFT calculations

DFT calculations were conducted using the Vienna Ab initio Simulation Package (VASP), with the exchange-correlation functional described by the

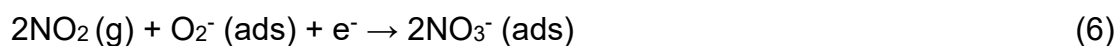
Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). Electron-ion interactions were modeled using the projector augmented-wave (PAW) method. A plane-wave cutoff energy of 400 eV was applied, and the Brillouin zone was sampled with a 2×3×1 Monkhorst-Pack k-point grid centered at the Gamma point. Convergence criteria for energy and force in self-consistent iterations were set to 10⁻⁴ eV and 0.05 eV Å⁻¹, respectively. To account for van der Waals (vdW) interactions, the DFT-D3 method was utilized. To evaluate the thermodynamic feasibility of the surface reaction processes, the Gibbs free energy changes (ΔG) were calculated. The ΔG value was calculated using the following equation (2):

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad (2)$$

Here, ΔE and ΔZPE denote the electronic energy difference and the difference in zero-point energy between the initial and final states, respectively. ΔS represents the entropy change, where T is the absolute temperature (so that $T\Delta S$ represents the entropic contribution).

Surface reactions

Reactions between WO₃-Ni-0.5 and the gas molecules are described by the following equations (3)-(6):



Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References:

- [1] Wu, X. et al. Bionic Olfactory Neuron with in-Sensor Reservoir Computing for Intelligent Gas Recognition. *Adv. Mater.* **37**, 2419159 (2025).
- [2] Deng, Y. et al. Elaborately Designed Intelligent Responsive Sensing Materials for Development of Flexible Gas Sensors. *Prog. Mater. Sci.* **156**, 101565 (2026).
- [3] Hu, C. et al. Chemiresistive Gas Sensors for Intelligent Sensing: Design Strategies, Emerging Applications and Future Challenges. *Chem. Soc. Rev.* **54**, 11302-11367 (2025).
- [4] Xie, W. et al. Synthesis of Ordered Mesoporous Metal Oxides by Solvent Evaporation-Induced Cooperative Assembly. *Nat. Protoc.* **21**, 987-1020 (2026).
- [5] Park, S. et al. Imparting Metal Oxides with High Sensitivity toward Light-Activated NO₂ Detection via Tailored Interfacial Chemistry. *Adv. Funct. Mater.* **33**, 2214008 (2023).
- [6] Ma, J. et al. Pt Nanoparticles Sensitized Ordered Mesoporous WO₃ Semiconductor: Gas Sensing Performance and Mechanism Study. *Adv. Funct. Mater.* **28**, 1705268 (2018).
- [7] Wang, O. et al. Electron-Deficient Pd Enabled by Single-Atom Alloy Drives Fast and Co-Resistant Hydrogen Sensing. *Adv. Funct. Mater.* **36**, e74682 (2026).
- [8] Yang, T. et al. Metal–Organic Framework Induced Prenucleation to Construct Solid Solution Semiconductor Metal Oxides with Synergistic Enhancement of Moisture Resistance and Gas Response. *ACS Sens.* **11**, 6784-6798 (2026).
- [9] Wang, W. et al. Orbital-Level Chemical Coding for Exclusive Detection of VOCs Gases in Chemiresistive Sensors. *Angew. Chem. Int. Ed.* **65**, e25408 (2026).
- [10] Liu, K. et al. Probing the Challenge of p-Type Semiconductors in Long-Chain VOC Detection: 3D Micro-Flower Zinc Cobaltate Heterojunction Sensors. *Adv. Sci.* **12**, e02646 (2025).
- [11] Pasupuleti, K. S. et al. High Performance Langasite Based SAW NO₂ Gas Sensor using 2D g-C₃N₄@TiO₂ Hybrid Nanocomposite. *J. Hazard. Mater.* **427**, 128174 (2022).
- [12] Nakamura, K. et al. van der Waals Interactions between Nonpolar Alkyl Chains and Polar Oxide Surfaces Prevent Catalyst Deactivation in Aldehyde Gas Sensing. *Nat. Commun.* **15**, 9211 (2024).
- [13] Li, M. et al. Highly Permeable CeO₂ Porous Hollow Microspheres with Multilevel Gas Channels for Rapid NH₃ Gas Response and Recovery Performance. *Energy Environ. Mater.* **9**, e70340 (2026).

- [14] Sun, Y.&Dai, S. High-Entropy Materials for Catalysis: A New Frontier. *Sci. Adv.* **7**, eabg1600 (2021).
- [15] Zhou, K. et al. Emerging 2D Metal Oxides: From Synthesis to Device Integration. *Adv. Mater.* **35**, 2207774 (2023).
- [16] Yuan, C. et al. Modeling Interfacial Interaction between Gas Molecules and Semiconductor Metal Oxides: A New View Angle on Gas Sensing. *Adv. Sci.* **9**, 2203594 (2022).
- [17] Ogbeide, O. et al. Inkjet-Printed rGO/Binary Metal Oxide Sensor for Predictive Gas Sensing in a Mixed Environment. *Adv. Funct. Mater.* **32**, 2113348 (2022).
- [18] Yang, X. et al. Functionalization of Mesoporous Semiconductor Metal Oxides for Gas Sensing: Recent Advances and Emerging Challenges. *Adv. Sci.* **10**, 2204810 (2023).
- [19] Ma, B. et al. A Zeolitic Octahedral Metal Oxide with Ultra-Microporosity for Inverse CO₂/C₂H₂ Separation at High Temperature and Humidity. *Angew. Chem. Int. Ed.* **61**, e202209121 (2022).
- [20] Zhang, Y., Zhang, X., Pang, Q.&Yan, J. Control of Metal Oxides' Electronic Conductivity through Visual Intercalation Chemical Reactions. *Nat. Commun.* **14**, 6130 (2023).
- [21] Kim, K.-W. et al. Low-Temperature, Universal Synthetic Route for Mesoporous Metal Oxides by Exploiting Synergistic Effect of Thermal Activation and Plasma. *Adv. Mater.* **36**, 2311809 (2024).
- [22] Wang, H. et al. Multifunctional High Entropy Alloys Enabled by Severe Lattice Distortion. *Adv. Mater.* **36**, 2305453 (2024).
- [23] Chen, Q. et al. Rapid Synthesis of Metastable Materials for Electrocatalysis. *Chem. Soc. Rev.* **54**, 4567-4616 (2025).
- [24] Li, M. et al. Rare-Earth-Induced Intermediate-Spin Co Centers in MnCo₂O_{4.5} for Sustainable Acidic Water Oxidation. *Journal of the American Chemical Society* **147**, 45680-45690 (2025).
- [25] Ye, C. et al. Activating Metal Oxides Nanocatalysts for Electrocatalytic Water Oxidation by Quenching-Induced Near-Surface Metal Atom Functionality. *Journal of the American Chemical Society* **143**, 14169-14177 (2021).
- [26] Ye, C. et al. Heterostructured Metal Oxides Realized by Quenching-Induced Structural Transformation. *Energy Environ. Sci.* **17**, 332-343 (2024).
- [27] Sen, S., Palabathuni, M., Ryan, K. M.& Singh, S. High Entropy Oxides: Mapping the Landscape from Fundamentals to Future Vistas: Focus Review. *ACS Energy Lett.* **9**, 3694-3718 (2024).
- [28] Wu, Y. et al. Synergistic Interplay of Ni Single Atoms and Neighboring Mn₂ Dual Atoms Enabling Selective Photocatalytic Reduction of CO₂ to Propane. *Angew. Chem. Int. Ed.* **65**, e21193 (2026).

- [29] Sun, Y. et al. Construction of a Built-in Electric Field in Mo-Doped Ni/WO₃ to Enhance Asymmetric Charge Distribution for Efficient Overall Water Splitting. *Chem. Sci.* **17**, 2210-2221 (2026).
- [30] Liu, F. et al. Excellent NO₂ Gas Sensor Based on the Oxygen Inhibiting Effect of Ni³⁺-Doped WO₃. *Colloids Surf. A* **666**, 131329 (2023).
- [31] Guo, P. et al. An All-Printed, Fast-Response Flexible Humidity Sensor Based on Hexagonal-WO₃ Nanowires for Multifunctional Applications. *Adv. Mater.* **35**, 2304420 (2023).
- [32] Zhou, Z. et al. Synergistic Interaction between Metal Single-Atoms and Defective WO₃-x Nanosheets for Enhanced Sonodynamic Cancer Therapy. *Adv. Mater.* **36**, 2311002 (2024).
- [33] Sun, J. et al. Single-Atom Ni on Tungsten Oxides Drives Hydrogen Spillover for Efficient Plastic Waste Upcycling. *ACS Catal.* **16**, 418-430 (2026).
- [34] Wang, J. et al. Metal Vacancies in Semiconductor Oxides Enhance Hole Mobility for Efficient Photoelectrochemical Water Splitting. *Nat. Catal.* **8**, 229-238 (2025).
- [35] Yan, G. et al. Noble-Metal-Free Ni-W Dual-Atom Sites with Bifunctional Synergy for Efficient Photocatalytic CO₂ Conversion. *Applied Catalysis B: Environment and Energy* **378**, 125535 (2025).
- [36] Jacobs, I. E. et al. Structural and Dynamic Disorder, Not Ionic Trapping, Controls Charge Transport in Highly Doped Conducting Polymers. *Journal of the American Chemical Society* **144**, 3005-3019 (2022).
- [37] Zhou, J. et al. Mobility Enhancement in Heavily Doped Semiconductors via Electron Cloaking. *Nat. Commun.* **13**, 2482 (2022).
- [38] Li, R. et al. Unraveling the Effect of Oxygen Vacancy on WO₃ Surface for Efficient NO₂ Detection at Low Temperature. *ACS Appl. Mater. Interfaces* **16**, 51738-51747 (2024).
- [39] Li, J. et al. Essential Role of Lattice Oxygen in Hydrogen Sensing Reaction. *Nat. Commun.* **15**, 2998 (2024).
- [40] Li, D., Zhao, L., Wang, J. & Yang, C. Tailoring the d-Band Center over Isomorphism Pyrite Catalyst for Optimized Intrinsic Affinity to Intermediates in Lithium–Oxygen Batteries. *Adv. Energy Mater.* **13**, 2204057 (2023).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (62304155, 62374115, 22508065), the 2025 “Spark” Project-Artificial Intelligence Empowerment Initiative, the Tongji University Medicine-X Interdisciplinary Research Initiative (2025-0674-YB-03), and the Fundamental

Research Funds for the Central University (22120230311). The work was conducted at Tongji University. The authors acknowledge the Experimental Center of Materials Science and Engineering at Tongji University.

Author Contributions

Y. W. Li and C. C. Ye contributed equally to this work. Y. W. Li: conceptualization, investigation, data curation, writing original draft. C. C. Ye: conceptualization, methodology, investigation, writing review and editing. H. M. Qiu: investigation, formal analysis. C. S. Pan: investigation, validation. J. Yang: conceptualization, supervision, funding acquisition, writing review and editing. J. Huang: conceptualization, supervision, funding acquisition, writing review and editing.

Competing interests

The authors declare no competing interests.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupportingInformationNatureCommunications.pdf](#)