

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

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Supplementary figures

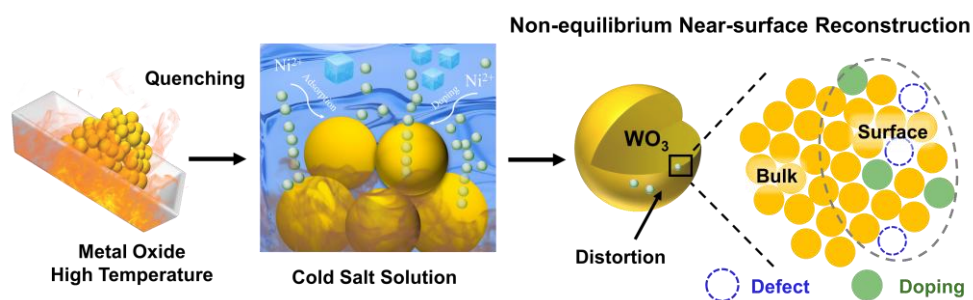


Figure S1. Schematic illustration of the thermochemical quenching process used to kinetically stabilize the reconstructed near-surface state of WO_3 -based sensing materials.

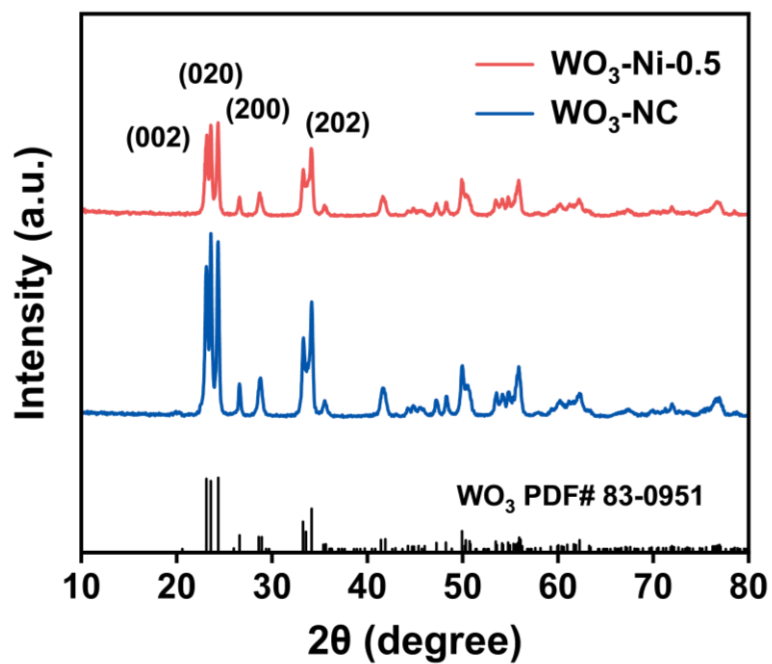


Figure S2. X-ray diffraction (XRD) patterns of $\text{WO}_3\text{-Ni-0.5}$ and $\text{WO}_3\text{-NC}$, confirming the preserved monoclinic phase of WO_3 after quenching.

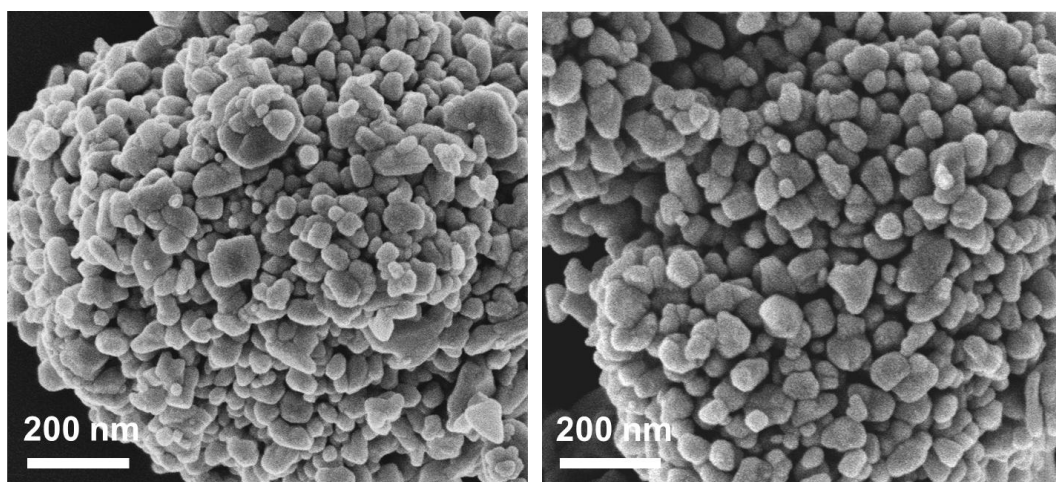


Figure S3. SEM images of WO₃-NC and WO₃-Ni-0.5.

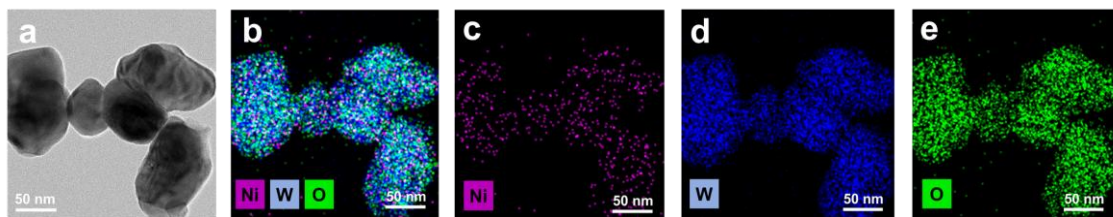


Figure S4. (a) Transmission electron microscopy (TEM) image of $\text{WO}_3\text{-Ni-0.5}$, showing the overall morphology of the quenched nanoparticles. (b) Overlay energy-dispersive X-ray (EDX) elemental map of Ni, W, and O, indicating a homogeneous spatial distribution of all elements across the nanoparticles. (c-e) Individual EDX elemental maps of Ni (c), W (d), and O (e).

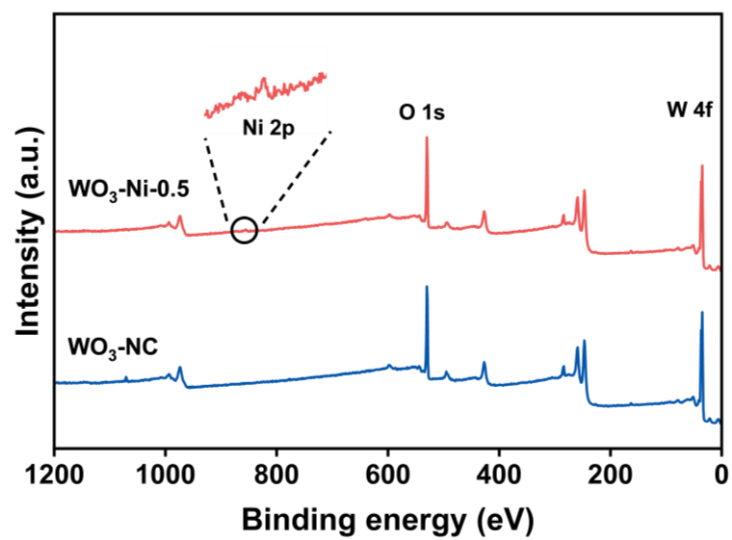


Figure S5. XPS full scan spectra of $\text{WO}_3\text{-Ni-0.5}$ and $\text{WO}_3\text{-NC}$.

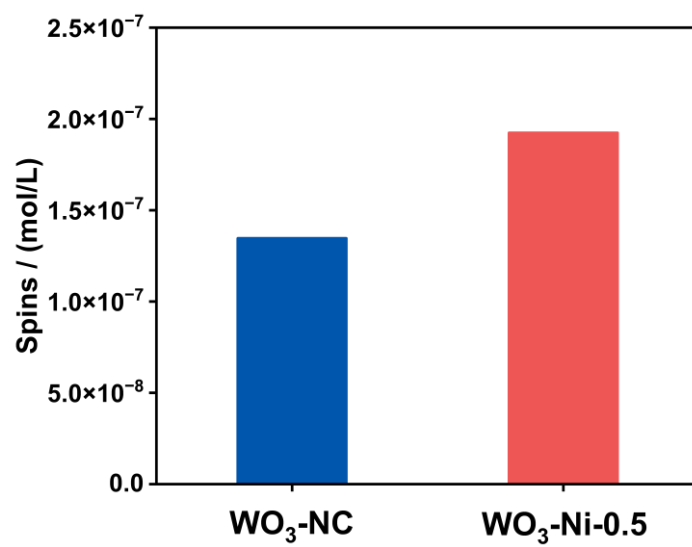


Figure S6. Oxygen vacancy concentrations in WO₃-Ni-0.5 and WO₃-NC as determined by electron paramagnetic resonance (EPR).

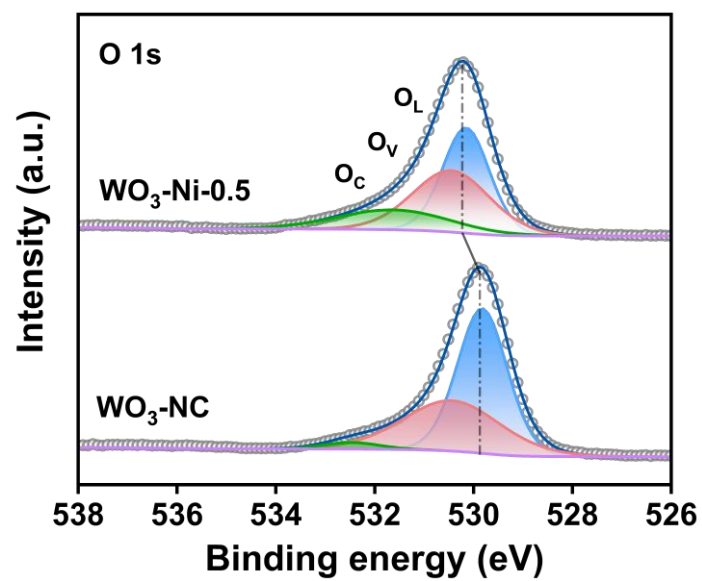


Figure S7. XPS spectra of the O 1s peak for $\text{WO}_3\text{-Ni-0.5}$ and $\text{WO}_3\text{-NC}$.

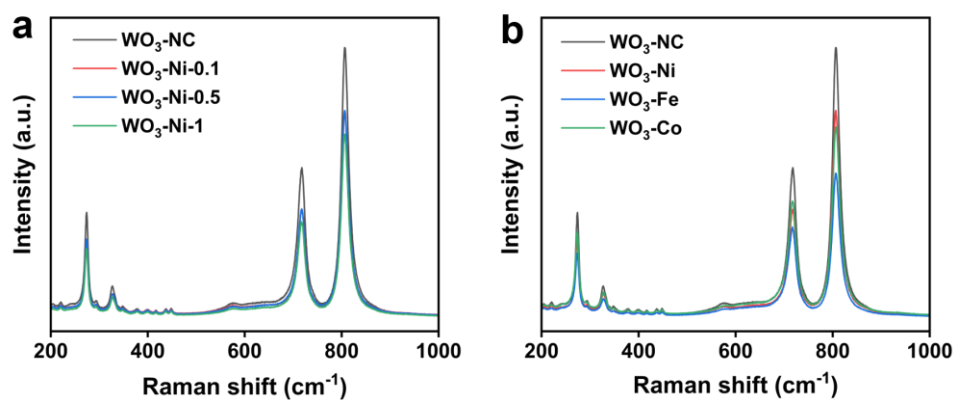


Figure S8. (a) Raman spectra of WO₃-NC and WO₃ with varying Ni concentrations during quenching. (b) WO₃ with different quenching elements at a concentration of 0.5 M.

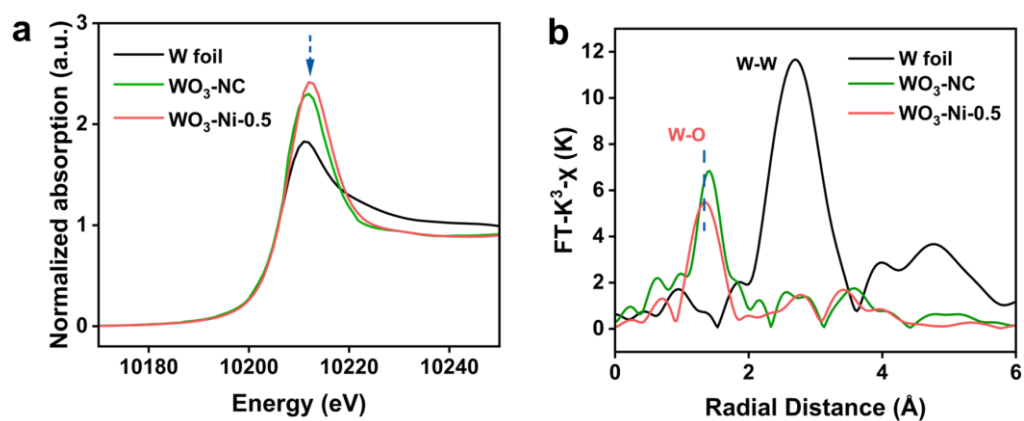


Figure S9. (a) W L₃-edge XANES spectra. **(b)** Fourier transformed $k^3\chi(R)$ W L₃-edge EXAFS for WO₃-Ni-0.5.

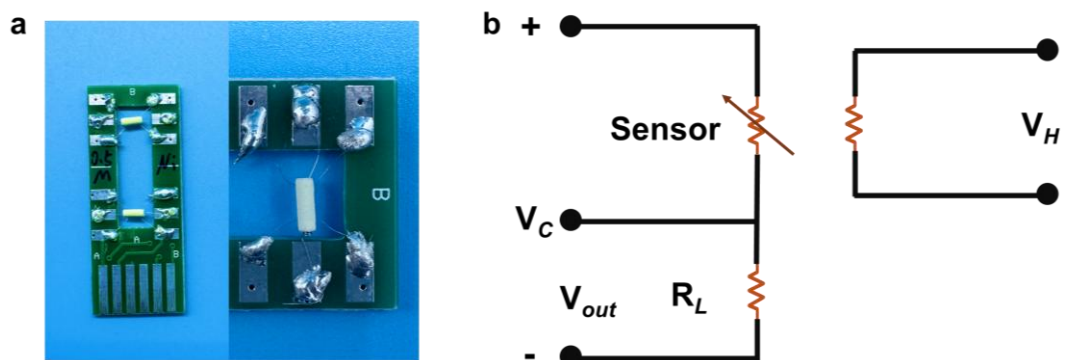


Figure S10. (a) Optical image of the gas sensing device. (b) Schematic diagram of the electric circuit for the gas sensing measurements.

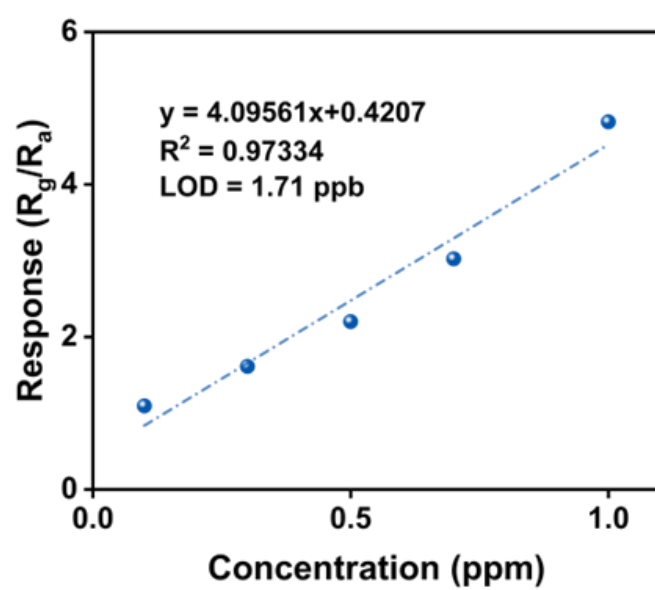


Figure S11. Linear fit of the response-concentration relationship.

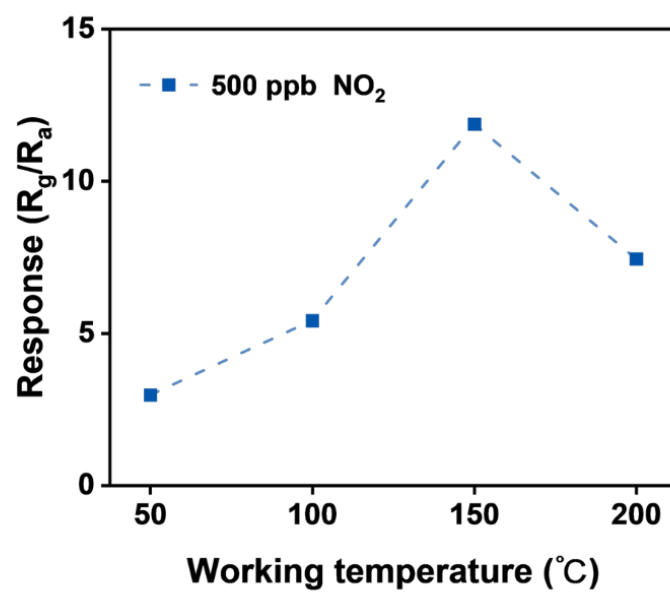


Figure S12. Sensor response to 500 ppb NO_2 at different temperatures.

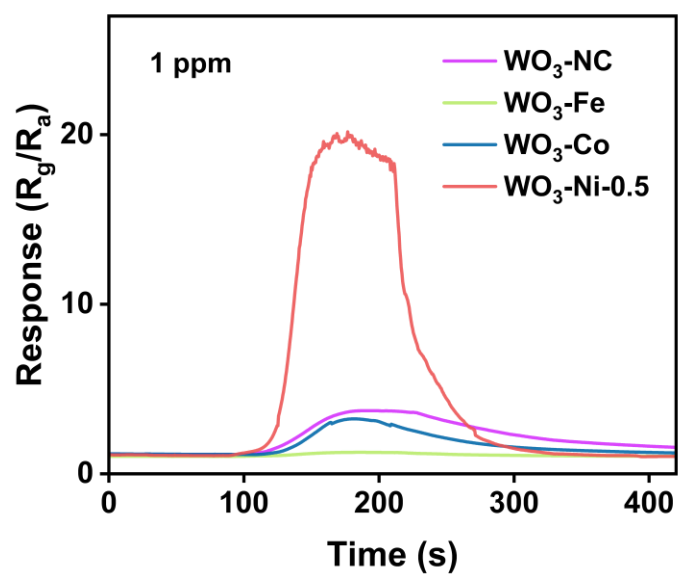


Figure S13. Responses of sensors with different quenching elements to 1 ppm NO₂.

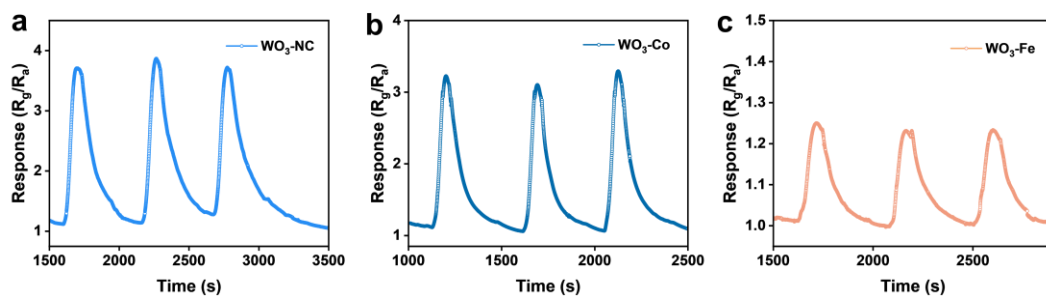


Figure S14. Repeated sensing responses of sensors with different quenching elements to 1 ppm NO₂ at 150 °C. (a) WO₃-NC; (b) WO₃-Co; (c) WO₃-Fe.

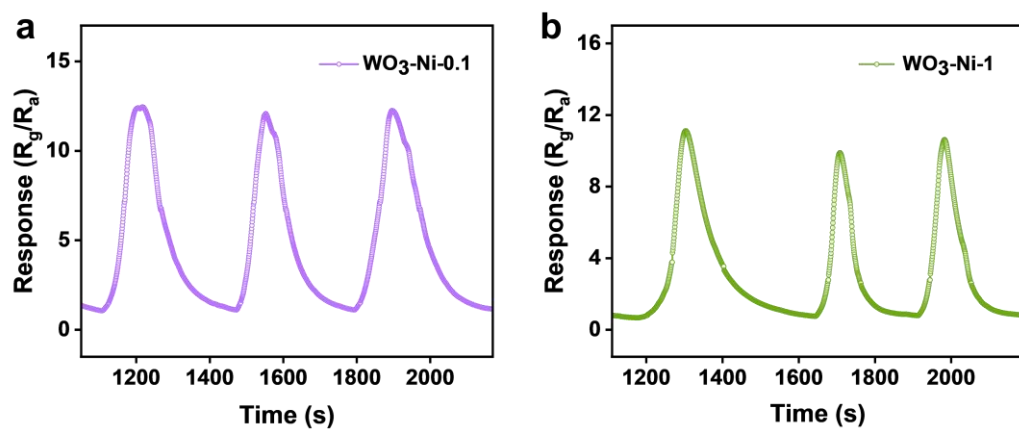


Figure S15. Repeated sensing responses of WO₃-Ni-0.1 (a) and WO₃-Ni-1 (b) to 1 ppm NO₂ at 150 °C.

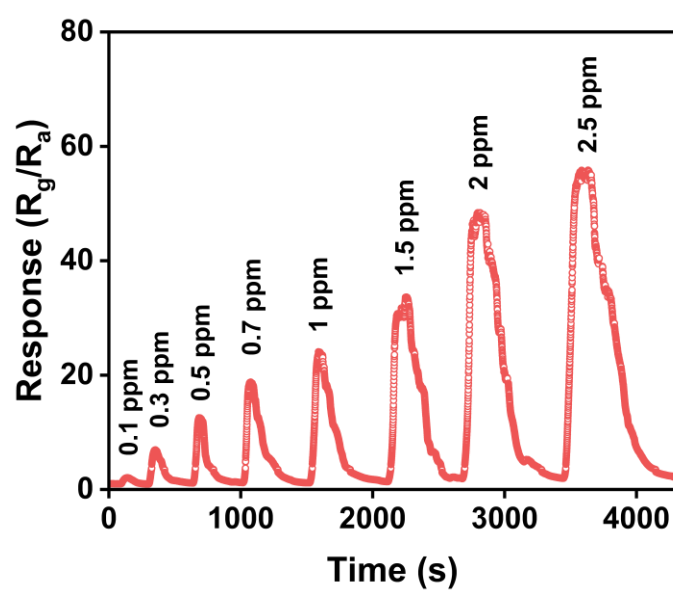


Figure S16. Response-recovery curves of the WO₃-Ni-0.5 based sensor to NO₂ at different concentrations (0.1-2.5 ppm) at 150 °C.

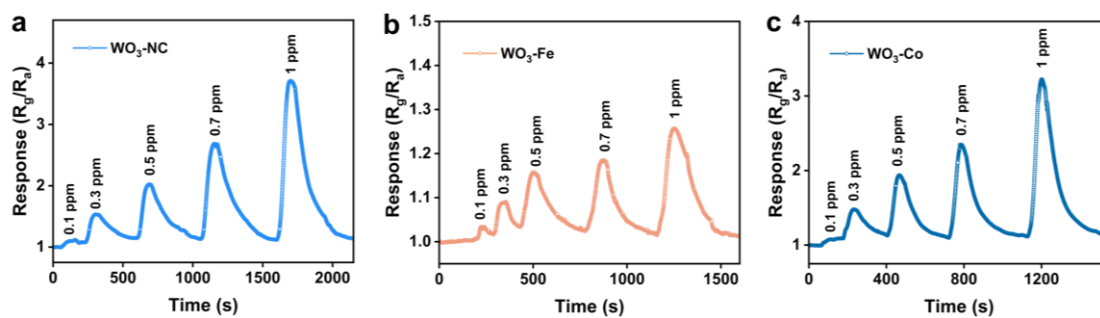


Figure S17. Response-recovery curve of sensors with different quenching elements to NO₂ at different concentrations (0.1-1 ppm) at 150 °C. (a) WO₃-NC; (b) WO₃-Fe; (c) WO₃-Co.

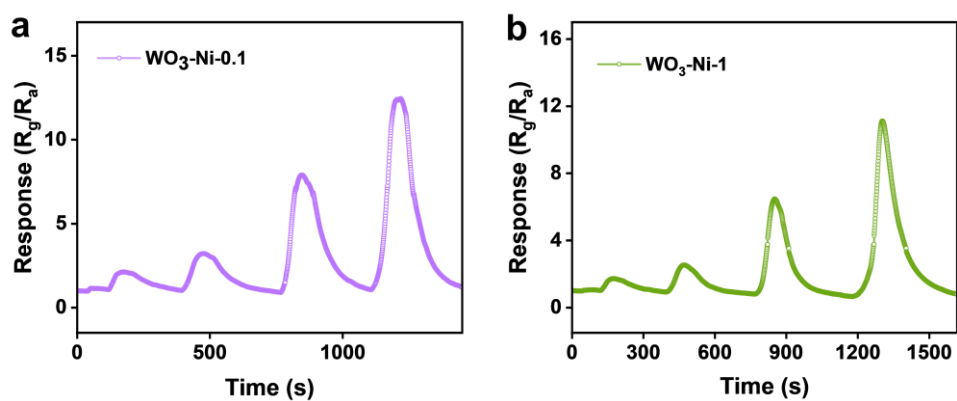


Figure S18. Response-recovery curve of sensors with varying Ni concentrations to NO₂ (0.1-1 ppm) at 150 °C. (a) WO₃-Ni-0.1; (b) WO₃-Ni-1.

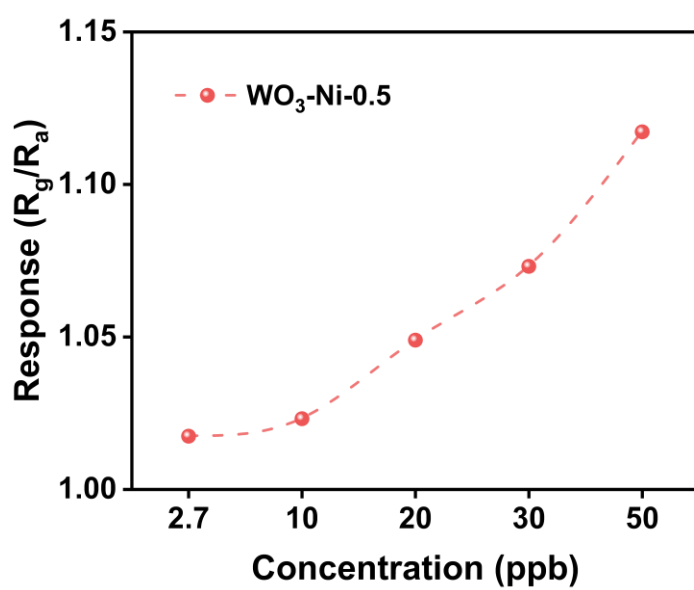


Figure S19. Response of $\text{WO}_3\text{-Ni-0.5}$ to different ppb-level NO_2 concentrations at $150\text{ }^\circ\text{C}$.

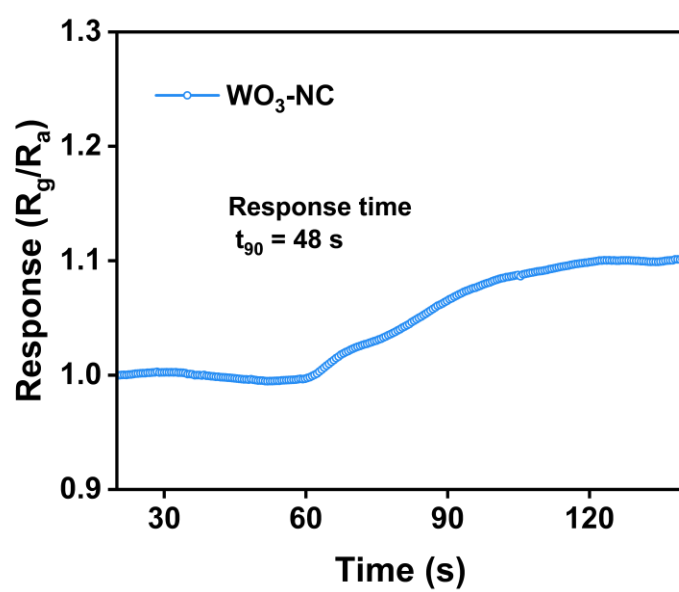


Figure S20. Response times of $\text{WO}_3\text{-NC}$ to 100 ppb NO_2 .

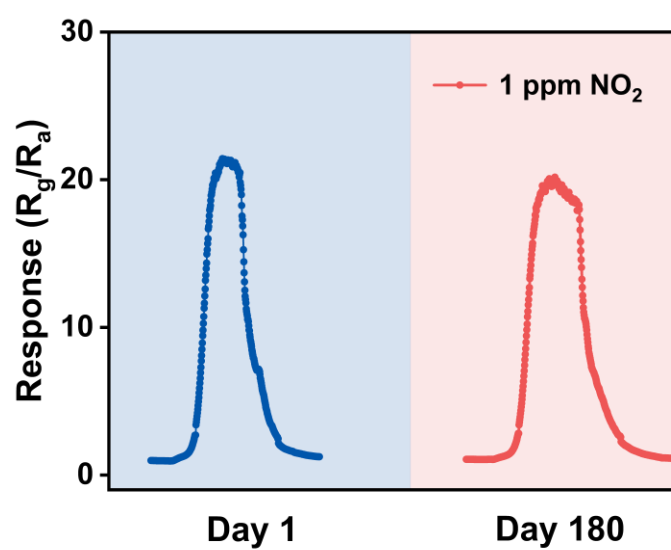


Figure S21. Normalized response of WO₃-Ni-0.5 sensor to 1 ppm NO₂ before and after being stored in ambient atmosphere for 180 days.

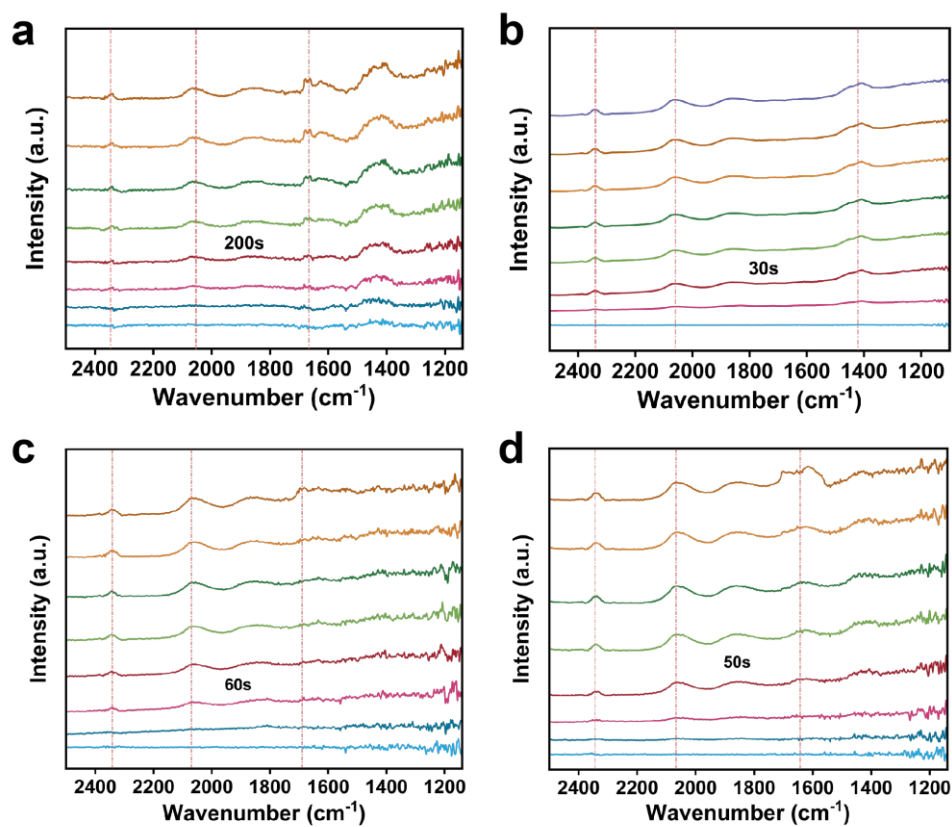


Figure S22. In situ FTIR spectra of NO₂ adsorbed on the surface of **(a, b)** WO₃-NC at room temperature and 150 °C, respectively, and **(c, d)** WO₃-Fe and WO₃-Co at 150 °C.

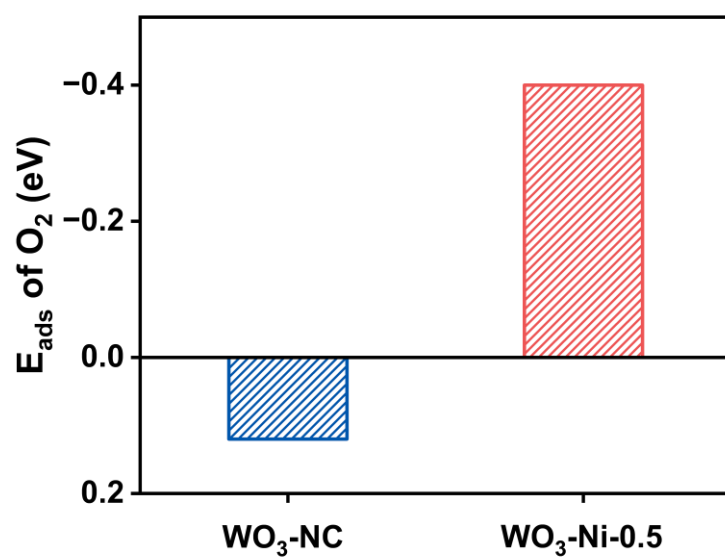


Figure S23. Adsorption energies of O₂ on WO₃-NC and WO₃-Ni-0.5.

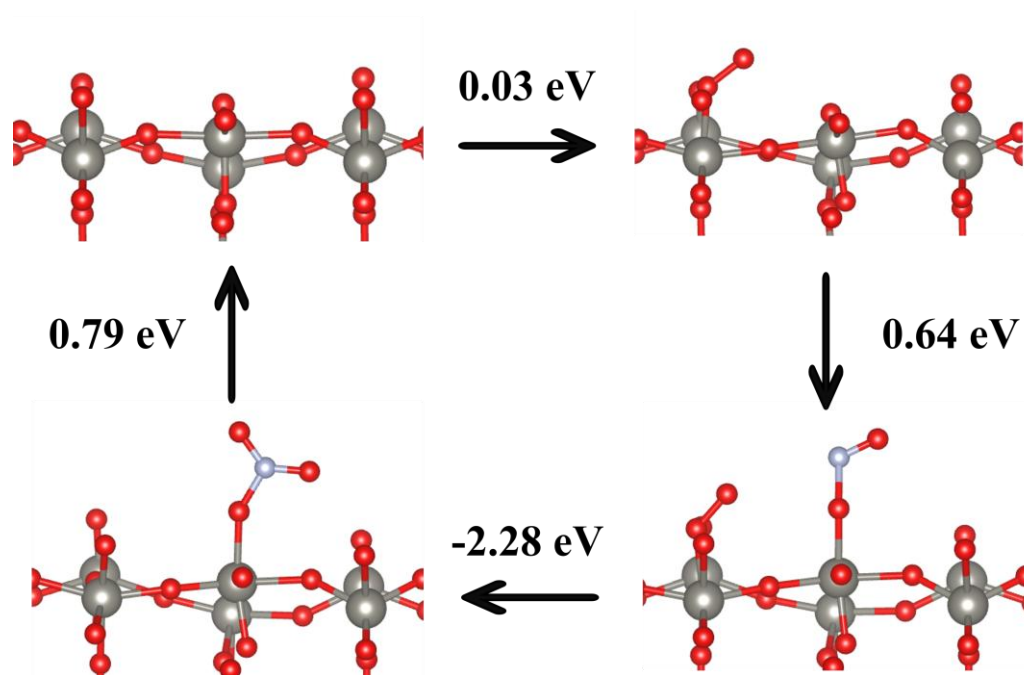


Figure S24. Catalytic pathway over $\text{WO}_3\text{-NC}$. (red spheres: oxygen atoms, gray spheres: tungsten atoms, white spheres: nitrogen atoms)

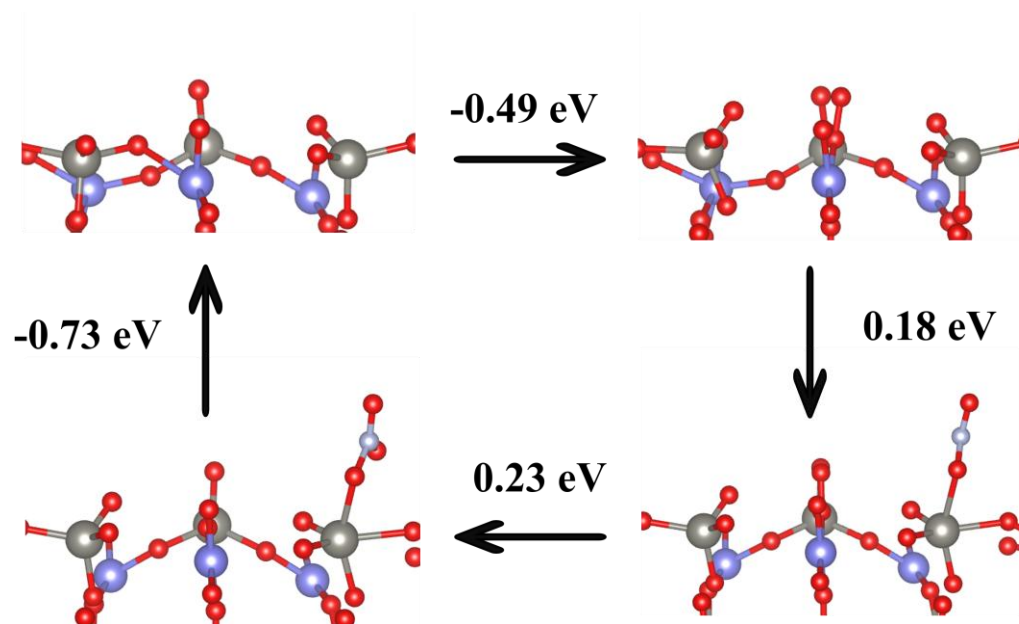


Figure S25. Catalytic pathway over $\text{WO}_3\text{-Ni-0.5}$. (blue spheres: nickel atom)

Table S1. Comparison of Reported NO₂ Sensing Materials

Sensing materials	Response (R_g/R_a)	Response time (s)	LOD (ppb)	Refs.
WO ₃ -Ni-0.5	21.3	3.5	0.052	This work
SnS ₂ /BP	5.2	18	100	[1]
Cu-Salphen-MOF	776%	150	280	[2]
LIG@Cu ₃ HHTP ₂	N/A	16	0.16	[3]
WO ₃ nanomesh	10	450	50	[4]
NiO/WO ₃	1.61	30	20	[5]
La ₂ O ₃ /WO ₃	N/A	31.8	4.4	[6]
In ₂ O ₃ N-40	N/A	5	10	[7]
TpPa-1/Cs ₂ PdBr ₆	30	71	40	[8]
SWCNT films	41.6%	14.2	0.16	[9]
WO ₃ /WS ₂	N/A	50	5	[10]

Response: Sensor response to 1 ppm NO₂.

Supplementary references

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- [10] Liang, Z. et al. Facile Fabrication of Nanoflower-Like WO_3/WS_2 Heterojunction for Highly Sensitive NO_2 Detection at Room Temperature. *J. Hazard. Mater.* **443**, 130316 (2023).