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Electronic Supplementary Information

Solution-Processed Metal Doping of Sub-3 nm SnO_2 Quantum Wires for Enhanced H_2S Sensing at Low Temperature

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Keywords: tin oxide; gas sensor; quantum wire; oxygen vacancy; metal atom doping

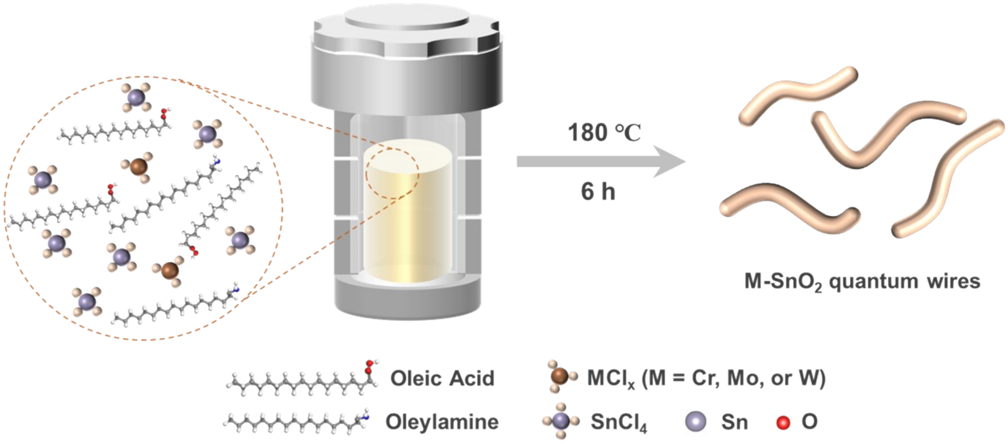

Fig.S1 Schematic diagram of the synthesis of metal-doped SnO_2 (M-SnO_2) quantum wires.

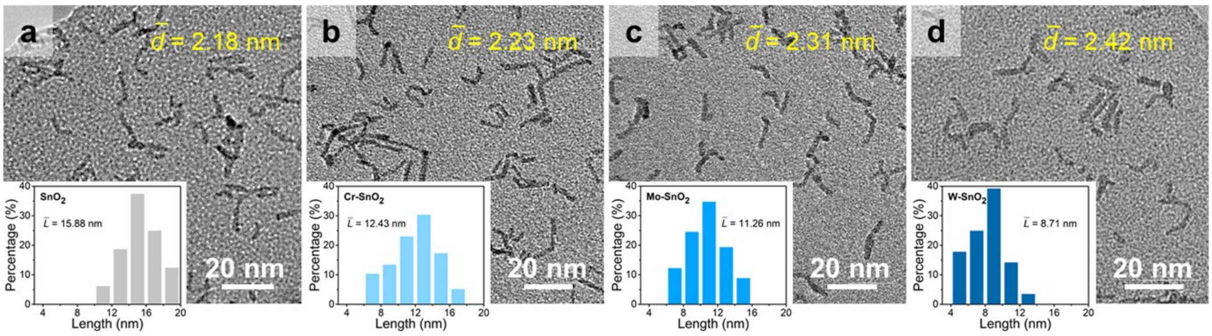

Fig. S2 TEM images of a) SnO_2, b) Cr-SnO_2, c) Mo-SnO_2, and d) W-SnO_2. Insets are histograms showing the distribution of length.

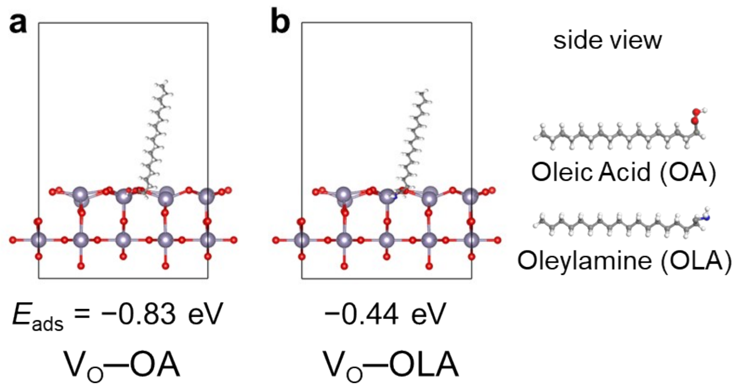

Fig. S3 Side view of model cell structure for DFT calculations of a) OA and b) OLA adsorption energy (E_{ads}) on SnO_2 (110) facets.

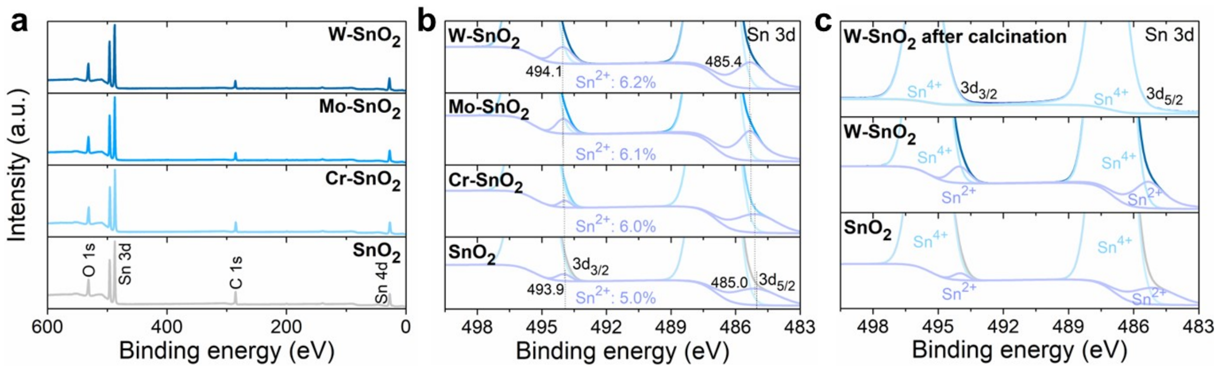

Fig. S4 a) XPS survey spectra and high-resolution Sn 3d spectra (enlarged Sn^{2+} peak area) of SnO_2, Cr-SnO_2, Mo-SnO_2, and W-SnO_2 b) before and c) after the heating treatment at 550 °C in air for 12 h.

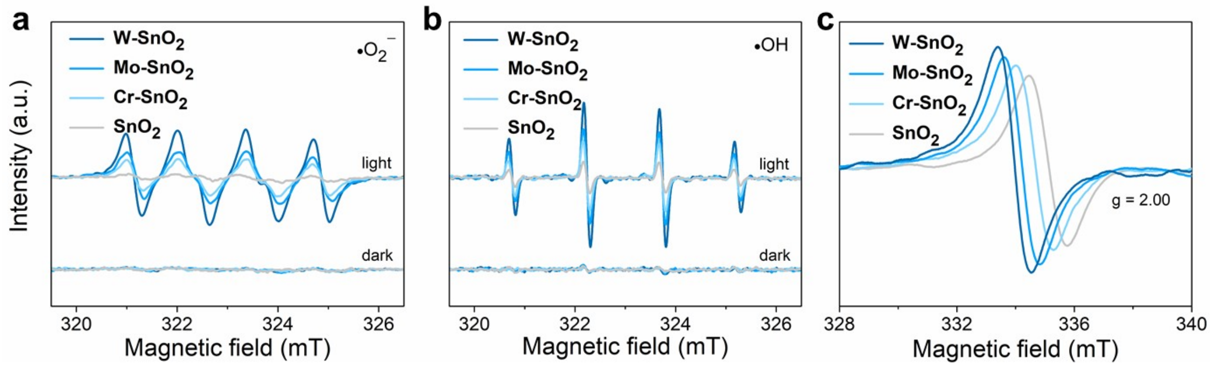

Fig. S5 ESR spectra of a) DMPO-•OH and b) DMPO-•O_2^- in aqueous and methanol dispersion of SnO_2, Cr-SnO_2, Mo-SnO_2, and W-SnO_2, respectively. c) EPR spectra of SnO_2, Cr-SnO_2, Mo-SnO_2, and W-SnO_2.

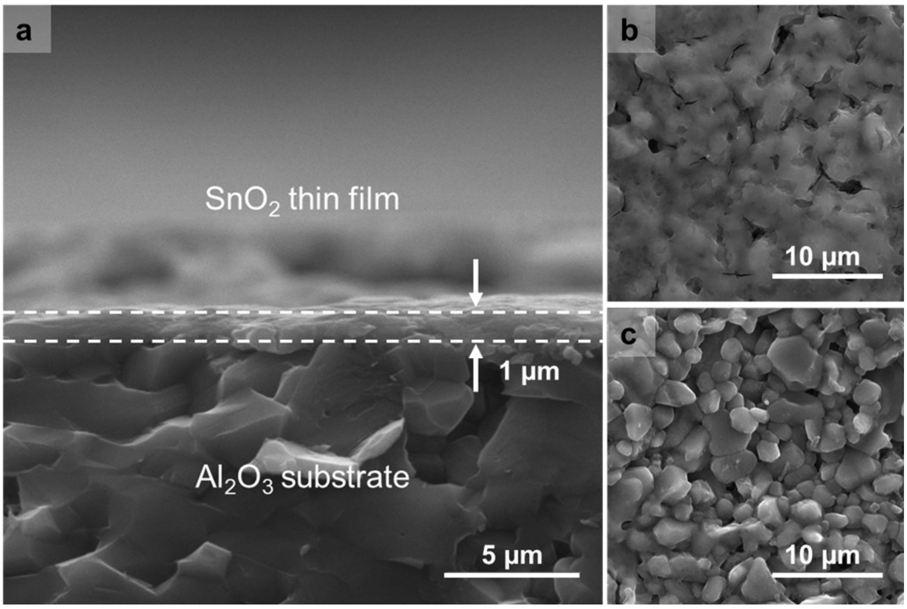

Fig. S6 a) Cross-sectional and b) top-view SEM images of SnO_2 thin film on Al_2O_3 ceramic substrate. c) SEM image of Al_2O_3 ceramic substrate.

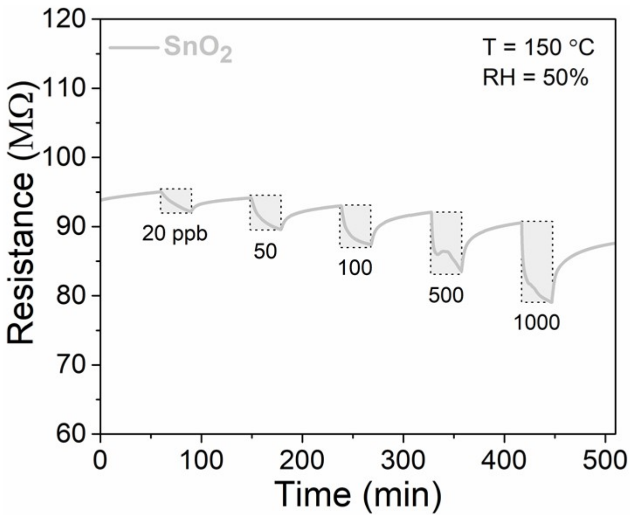

Fig. S7 A typical H_2S sensing curve of SnO_2 from 20 to 1,000 ppb H_2S at the optimized operation temperature (150 ℃).

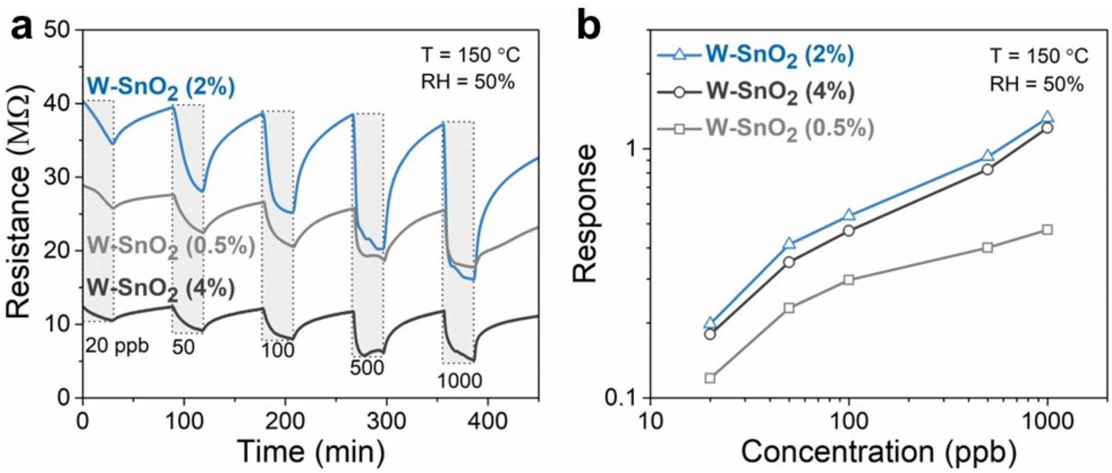

Fig. S8 Gas-sensing curves and the corresponding response toward H_2S of W-SnO_2-based sensors prepared with different W doping contents.

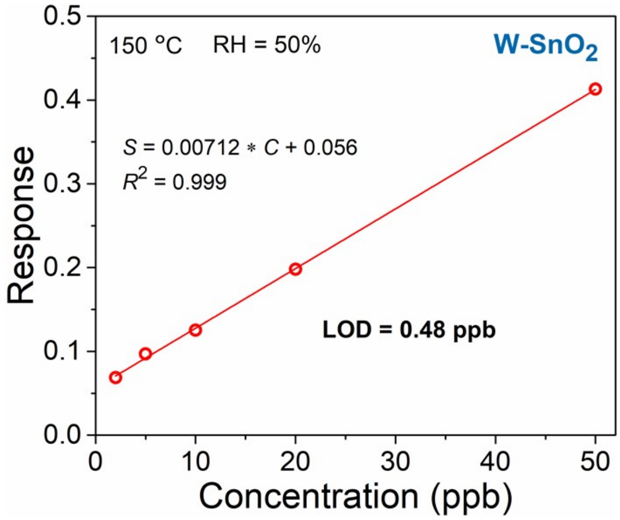

Fig. S9 A plot of sensor response against the concentration of H_2S.

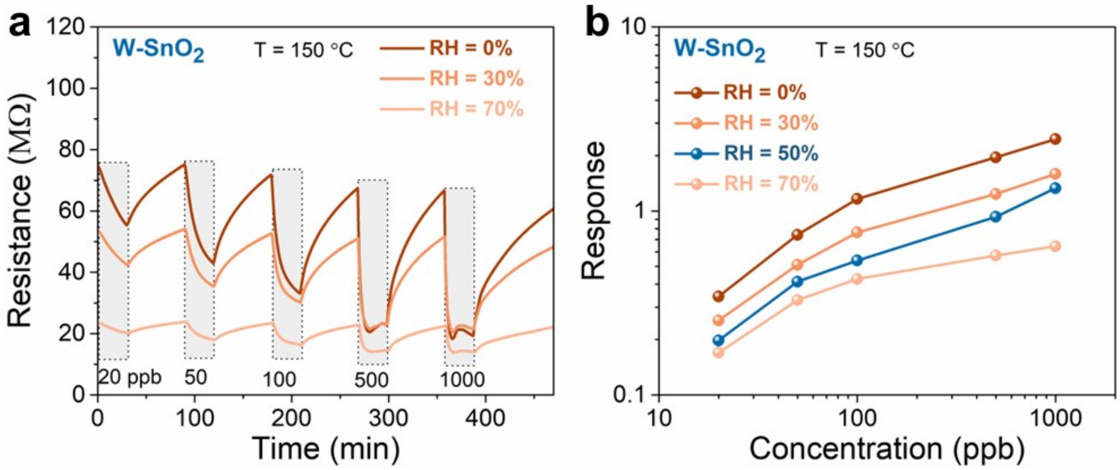

Fig. S10 Effect of humidity on the sensing performance of W-SnO_2-based gas sensor: a) Gas-sensing curve and b) sensing response.

Table S1 Molar ratio of doped metal in SnO_2 (M/Sn) obtained by STEM–EDS mapping.

	Cr-SnO_2	**Mo-SnO_2**	**W-SnO_2**
molar ratio of M/Sn	1.71 at.%	1.79 at.%	2.03 at.%

Table S2 Comparison of H_2S gas sensor performances at low temperatures.

Sample	**Temperature (℃)**	**H_2S Concentration (ppm)**	**Response[a]**	**LOD[b] (ppb)**	**Ref.**
W-SnO_2 QWs[c]	150	0.001 0.1 1.0	0.038 0.538 1.330	0.48	**This work**
La/ZnO	150	5.0	175.3	50.0	1
CuO/NiO nanowall	133	5.0	35.9	0.5	2
WO_3 QDs[d]	80	10.0	6.0	56.0	3
$BiVO_4$	75	5.0	3.9	62.5	4
In_2O_3 QDs[d]	37	0.5	3.4	4.4	5
SnO_2/rGO[e]/PANI[f]	RT[g]	5.0	3.2	50.0	6
CuO/TiO_2	RT[g]	100	0.88	3000	7
WO_3-Bi_2WO_6	RT[g]	0.05	3.4	2	8
Cu-doped In_2O_3	250	50	340.7	1000	9

[a] Response = $R_a/R_g - 1$; [b] LOD = limit of detections; [c] QWs = quantum wires; [d] QDs = quantum dots; [e] rGO = reduced graphene oxide; [f] PANI = polyaniline; [g] RT = room temperature

Table. S3 Properties of the interfering gas molecules.[10, 11]

Gas	H_2S	CH_4	CO	H_2	toluene	FA[a]
Broken bond	HS−H	CH_3−H	C−O	H−H	CH_3−OC_6H_5	H−CHO
Bond energy ($kJ\ mol^{-1}$)	381.0	431.0	1076.5	436.0	273.2	368.40

[a] FA = formaldehyde

References

1. Y. Zhang, C. Wang, L. Zhao, F. Liu, X. Sun, X. Hu and G. Lu, *Sens. Actuators B Chem.*, 2021, **334**, 129514.
2. L. Sui, T. Yu, D. Zhao, X. Cheng, X. Zhang, P. Wang, Y. Xu, S. Gao, H. Zhao, Y. Gao and L. Huo, *J. Hazard. Mater.*, 2020, **385**, 121570.
3. H. Yu, Z. Song, Q. Liu, X. Ji, J. Liu, S. Xu, H. Kan, B. Zhang, J. Liu, J. Jiang, L. Miao and H. Liu, *Sens. Actuators B Chem.*, 2017, **248**, 1029-1036.
4. C. Li, X. Qiao, J. Jian, F. Feng, H. Wang and L. Jia, *Chem. Eng. J.*, 2019, **375**, 121924.
5. S. Yang, Z. Song, N. Gao, Z. Hu, L. Zhou, J. Liu, B. Zhang, G. Zhang, S. Jiang, H.-Y. Li and H. Liu, *Sens. Actuators B Chem.*, 2019, **286**, 22-31.
6. D. Zhang, Z. Wu and X. Zong, *Sens. Actuators B Chem.*, 2019, **289**, 32-41.
7. H. He, C. Zhao, J. Xu, K. Qu, Z. Jiang, Z. Gao and Y. Y. Song, *ACS Sens.*, 2021, **6**, 3387-3397.
8. C. Zhang, K. Wu, H. Liao and M. Debliquy, *Chem. Eng. J.*, 2022, **430**, 132813.
9. Y. Zhang, S. Han, M. Wang, S. Liu, G. Liu, X. Meng, Z. Xu, M. Wang and G. Qiao, *J. Adv. Ceram.*, 2022, **11**, 427-442.
10. Z. S. Hosseini, A. I. zad and A. Mortezaali, *Sens. Actuators B Chem.*, 2015, **207**, 865-871.
11. Y.-R. Luo, *Handbook of bond dissociation energies in organic compounds*, CRC Press, Boca Raton London New York Washington, D.C., 2002.