

Supplementary Data

Cr Doping WO₃ Nanofibers Enriched with Surface Oxygen Vacancies for Highly Sensitive Detection of 3-Hydroxy-2-Butanone Biomarker

Zhengyou Zhu,^a Lijun Zheng,^a Shizheng Zheng,^a Jian Chen,^a Minghui Liang,^b Yongtao Tian,^c and Dachi Yang ^{*a}

^a Tianjin Key Laboratory of Optoelectronic Sensor and Sensing Network Technology and Department of Electronics, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China

^b Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing, 100190, P. R. China

^c School of Physics and Engineering and Key Laboratory of Materials Physics, Ministry of Education, Zhengzhou University, Zhengzhou 450001, P. R. China

* Corresponding E-mail: yangdachi@nankai.edu.cn

Outline

Fig. S1. Schematic diagram of synthetic procedure of the Cr doped WO₃ NFs. PVP/W/Cr precursor NFs were prepared via electrospinning followed by calcination at 500 °C to obtain Cr doped WO₃ NFs.

Fig. S2 TEM images of pristine and 2% Cr/WO₃ multiple NFs. Pristine WO₃ NFs show uniform surface morphology while 2% Cr/WO₃ NFs contain fiber stems and attached particles on the fiber.

Fig. S3 SEM images of 0.5% (a), 1% (b) and 3% wt (c) Cr/WO₃ NFs. 0.5% Cr/WO₃ NFs have similar morphology feature relative to pristine WO₃ NFs, while those with 1% and 3% Cr dopants contain a fiber stem and attached particles similar to

2% Cr/WO₃ NFs.

Fig. S4. N₂ adsorption/desorption isotherms of the pristine and 2% Cr/WO₃ NFs.

Fig. S5 (a) Full XPS spectrum of 2% Cr/WO₃ NFs; (b) High-resolution Cr 2p spectrum of 2% Cr/WO₃ NFs, where two peaks at higher and lower binding energies are assigned to Cr 2p_{1/2} and Cr 2p_{2/3}, respectively.

Fig. S6. Gas sensitivities of the 2% Cr/WO₃ NFs sensor as a function of the operating temperature to 5 ppm 3H-2B (a) and 100 ppm acetone (b), which show the optimal working temperature at 140 °C and 260 °C, respectively.

Table S1 Comparison of the gas-sensing performance of various modified WO₃ sensors to VOCs.

Table S2 Selectivity investigation of the 2% Cr/WO₃ NFs sensor in a gas mixture at 140 °C.

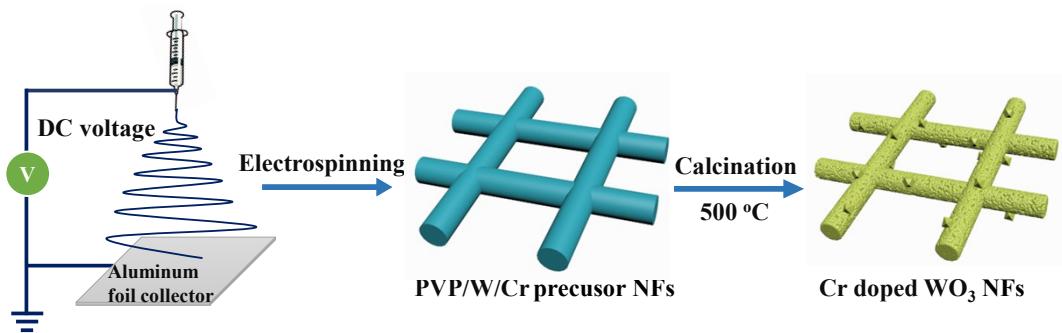


Fig. S1 Schematic diagram of synthetic procedure of the Cr/ WO_3 NFs. PVP/W/Cr precursor NFs were prepared via electrospinning followed by calcination at 500 °C to obtain Cr/ WO_3 NFs.

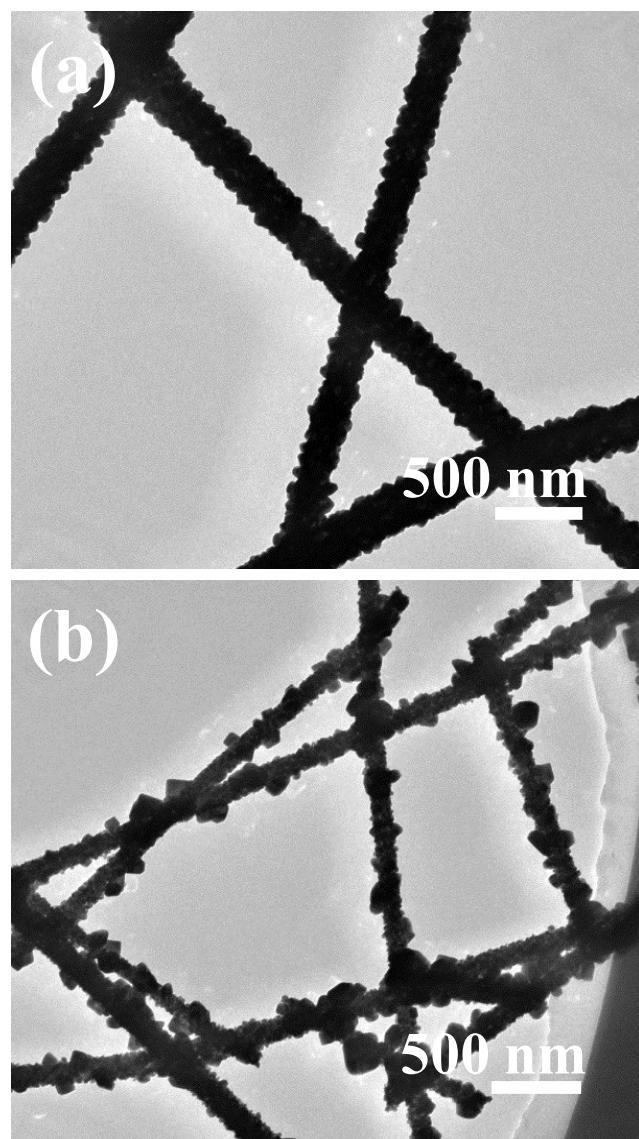


Fig. S2 TEM images of pristine and 2% Cr/ WO_3 multiple NFs. Pristine WO_3 NFs show uniform surface morphology while 2% Cr/ WO_3 NFs contain fiber stems and attached particles on the fiber.

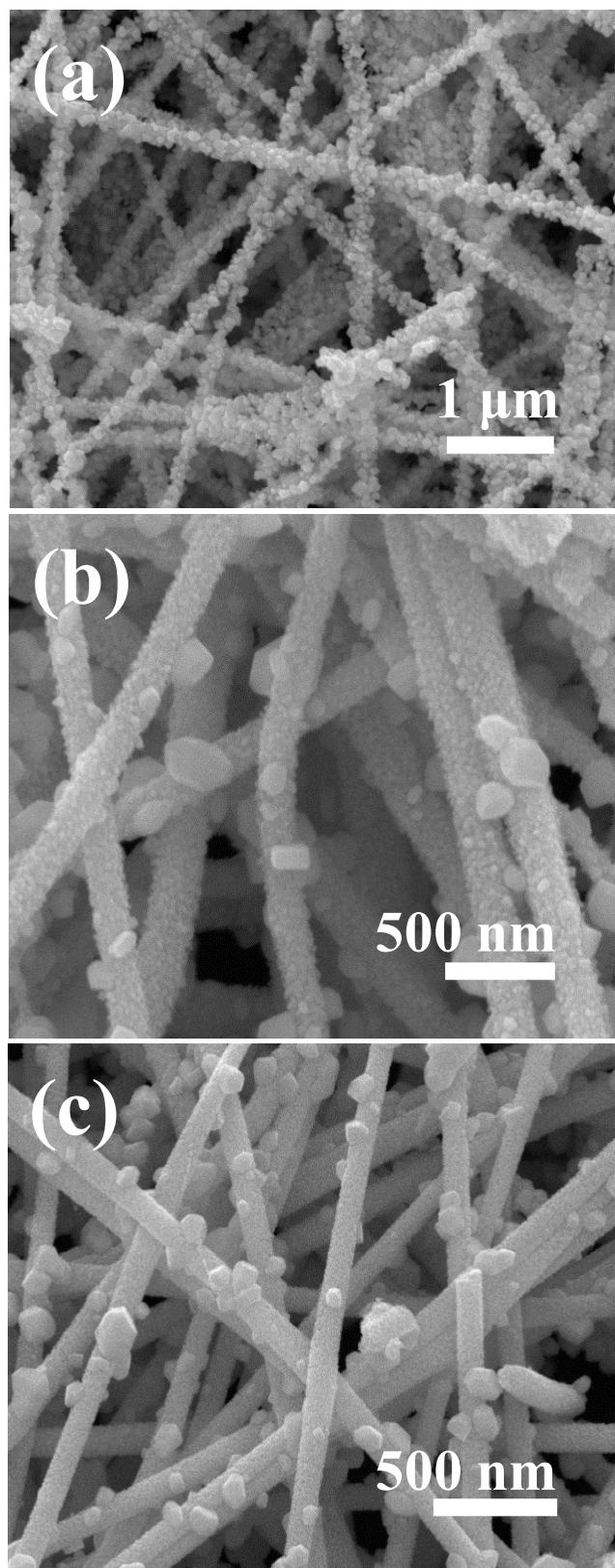


Fig. S3 SEM images of 0.5% (a), 1% (b) and 3% wt (c) Cr/WO₃ NFs. 0.5% Cr/WO₃ NFs have similar morphology feature relative to pristine WO₃ NFs, while those with 1% and 3% Cr dopants contain a fiber stem and attached particles similar to 2% Cr/WO₃ NFs.

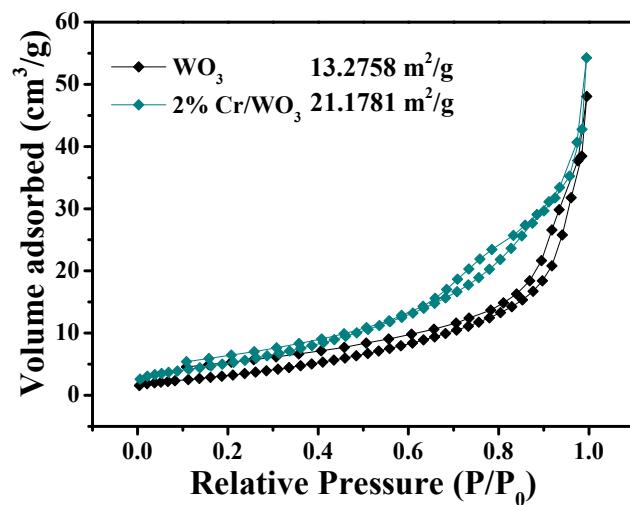


Fig. S4. N₂ adsorption / desorption isotherms of the pristine and 2% Cr/WO₃ NFs.

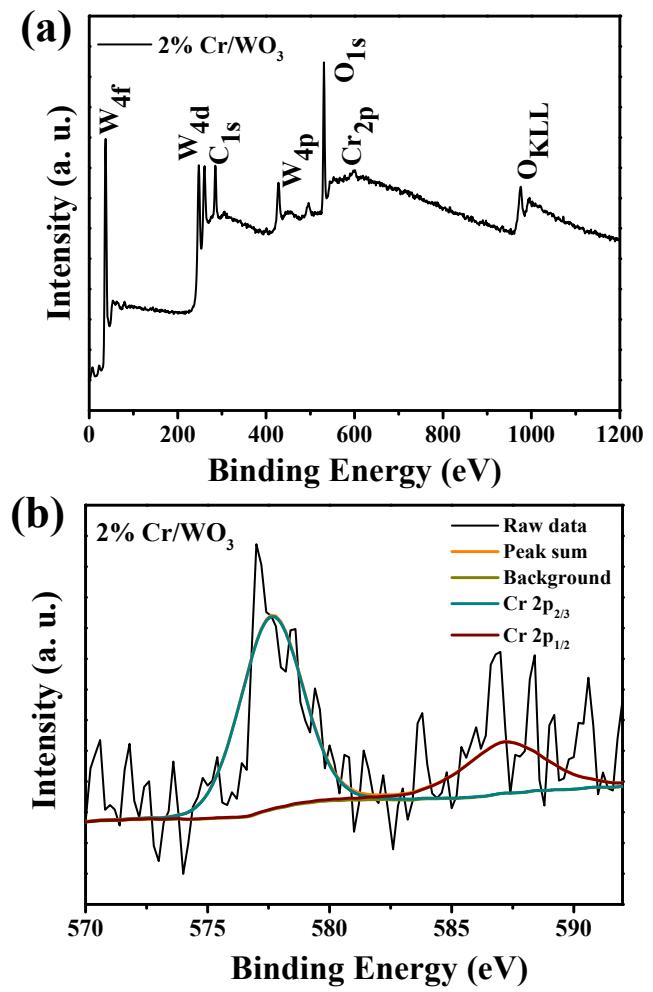


Fig. S5 (a) Full XPS spectrum of 2% Cr/WO₃ NFs. (b) High-resolution Cr 2p spectrum of 2% Cr/WO₃ NFs, where two peaks at higher and lower binding energies are assigned to Cr 2p_{1/2} and Cr 2p_{3/2}, respectively.

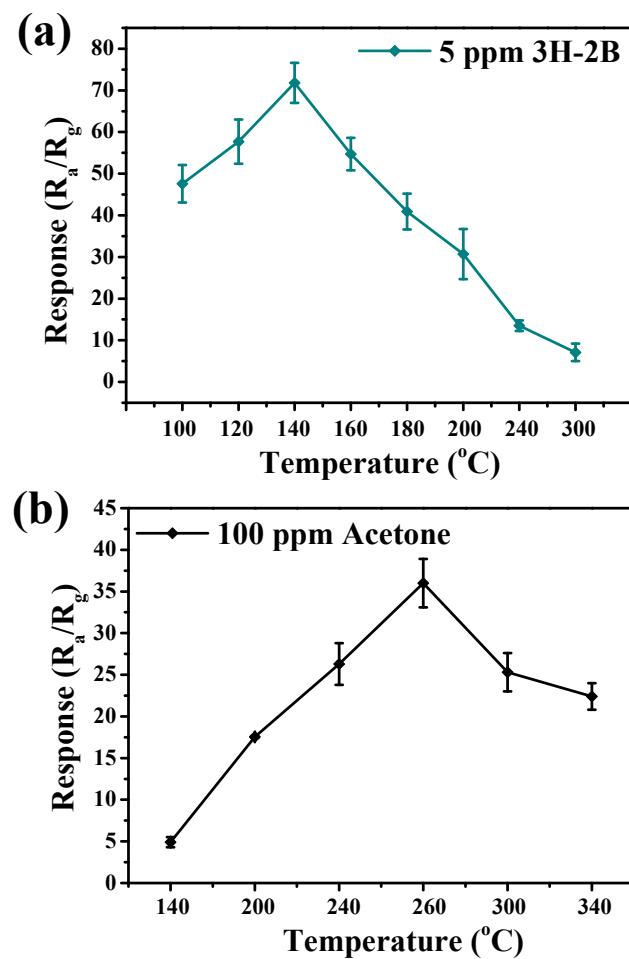


Fig. S6. Gas sensitivities of the 2% Cr/WO₃ NFs sensor as a function of the operating temperature to 5 ppm 3H-2B (a) and 100 ppm acetone (b), which show the optimal working temperature at 140 °C and 260 °C, respectively.

Table S1 Comparison of the gas-sensing performance of various modified WO_3 sensors to VOCs

Samples	Gases	C (ppm)	Temp. (°C)	$S(R_a/R_g)$	Detection limit (ppm)	Refs.
Cu-doped WO_3 hollow fibers	Acetone	20	300	6.43	0.25	[1]
C-doped WO_3 hollow sphere	Acetone	10	300	~11	0.2	[2]
Co-doped WO_3 flower-like nanostructures	Acetone	50	350	69	1	[3]
Cu-doped WO_3	Trimethylamine	10	290	49.6	0.5	[4]
Rh_2O_3 -functionalized WO_3 nanofibers	Acetone	5	350	41.5	0.1	[5]
Pt-Functionalized WO_3 hemitube	Acetone	2	300	4.11	0.12	[6]
Pd functionalized WO_3 nanofibers	Toluene	1	350	5.5	0.12	[7]
Au functionalized WO_3	<i>n</i> -butanol	10	250	63.6	/	[8]
Pd-loaded WO_3 nanofiber	Acetone	5	400	28.9	0.1	[9]
Cr/ WO_3 NFs	3H-2B	5	140	67	0.05	This work

References

- [1] X. Bai, H. Ji, P. Gao, Y. Zhang, X. Sun, *Sens. Actuators, B* 2014, **193**, 100-106.
- [2] J. Y. Shen, L. Zhang, J. Ren, J. C. Wang, H. C. Yao, Z. J. Li, *Sens. Actuators, B* 2017, **239**, 597-607.
- [3] Z. Liu, B. Liu, W. Xie, H. Li, R. Zhou, Q. Li, T. Wang, *Sens. Actuators, B* 2016,

235, 614-621.

- [4] S. Zhu, X. Liu, Z. Chen, C. Liu, C. Feng, J. Gu, Q. Liu, D. Zhang, *J. Mater. Chem.* 2010, **20**, 9126-9132.
- [5] N. H. Kim, S. J. Choi, S. J. Kim, H. J. Cho, J. S. Jang, W. T. Koo, M. Kim, I. D. Kim, *Sens. Actuators, B* 2016, **224**, 185-192.
- [6] S. J. Choi, I. Lee, B. H. Jang, D. Y. Youn, W. H. Ryu, C. O. Park, I. D. Kim, *Anal. Chem.* 2013, **85**, 1792-1796.
- [7] N. H. Kim, S. J. Choi, D. J. Yang, J. Bae, J. Park, I. D. Kim, *Sens. Actuators, B* 2014, **193**, 574-581.
- [8] X. Yang, V. Salles, Y. V. Kaneti, M. Liu, M. Maillard, C. Journet, X. Jiang, A. Brioude, *Sens. Actuators, B* 2015, **220**, 1112-1119.
- [9] S. J. Choi, S. J. Kim, H. J. Cho, J. S. Jang, Y. M. Lin, H. L. Tuller, G. C. Rutledge, I. D. Kim, *Small* 2016, **12**, 911-920.

Table S2 Selectivity investigation of the 2% Cr/WO₃ NFs sensor in a gas mixture at 140 °C.

Gases	Average Sensitivity (R_a/R_g)
10 ppm 3H-2B	135.2
10 ppm + Interfering gas mixture	138.7
5 ppm 3H-2B	71.5
5 ppm + Interfering gas mixture	67.2
0.5 ppm 3H-2B	18.9
0.5 ppm 3H-2B + Interfering gas mixture	20.1

Interfering gas mixture: 100 ppm ethanol + 100 ppm acetone + 100 ppm toluene + 100 ppm benzaldehyde