

Electronic Supplementary Information (ESI)

A novel approach for green synthesis of WO₃ nanomaterials and their highly selective chemical sensing properties

Vardan Galstyan,^{*a} Nicola Poli,^a Annalisa D'Arco,^{bc} Salvatore Macis,^c Stefano Lupi,^{cd} Elisabetta Comini^a

^a Sensor Lab, Department of Information Engineering, University of Brescia, Via Valotti 9, 25133 Brescia, Italy

^b INFN - National Institute of Nuclear Physics section Rome, P.le A. Moro 2, 00185 Rome, Italy

^c Physics Department, University of Rome 'La Sapienza', P.le A. Moro 5, 00185 Rome, Italy

^d INFN-LNF Via E. Fermi 40, 00044 Frascati, Italy

*E-mail address: vardan.galstyan@unibs.it

Results

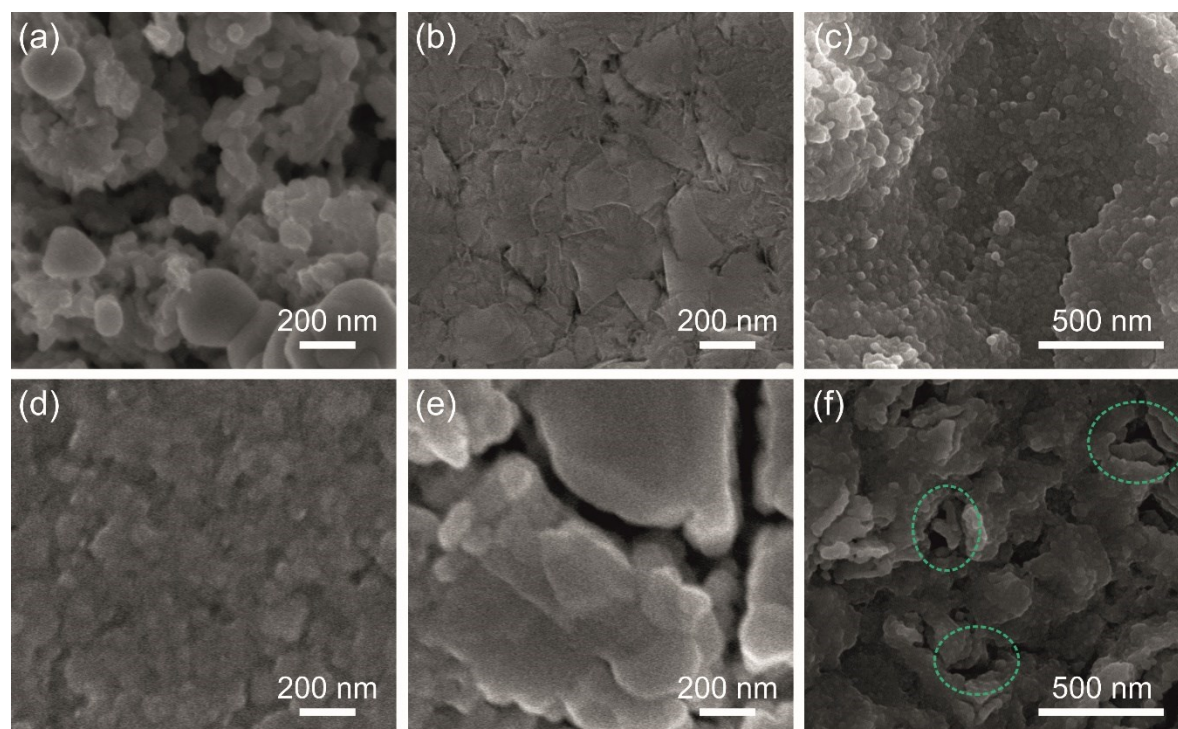


Fig. S1 Morphological analysis of samples carried out by FESEM.: (a) sample prepared in 0.3 mol L⁻¹ NaCl containing H₂O at 180 °C for 20 h, (b) sample prepared in distilled H₂O at 160 °C for 20 h (the preparation regimes of WO₃-1 sample without the use of NaCl), c) WO₃-1, (d) sample obtained under the exposure to H₂O vapor when the temperature of the reactor was 110 °C and the treatment time was 30 h, (e) sample prepared under the exposure to H₂O vapor at 140 °C for 35 h, (f) WO₃-2, where the big porous regions observed on the surface of structure are shown with the green dashed lines.

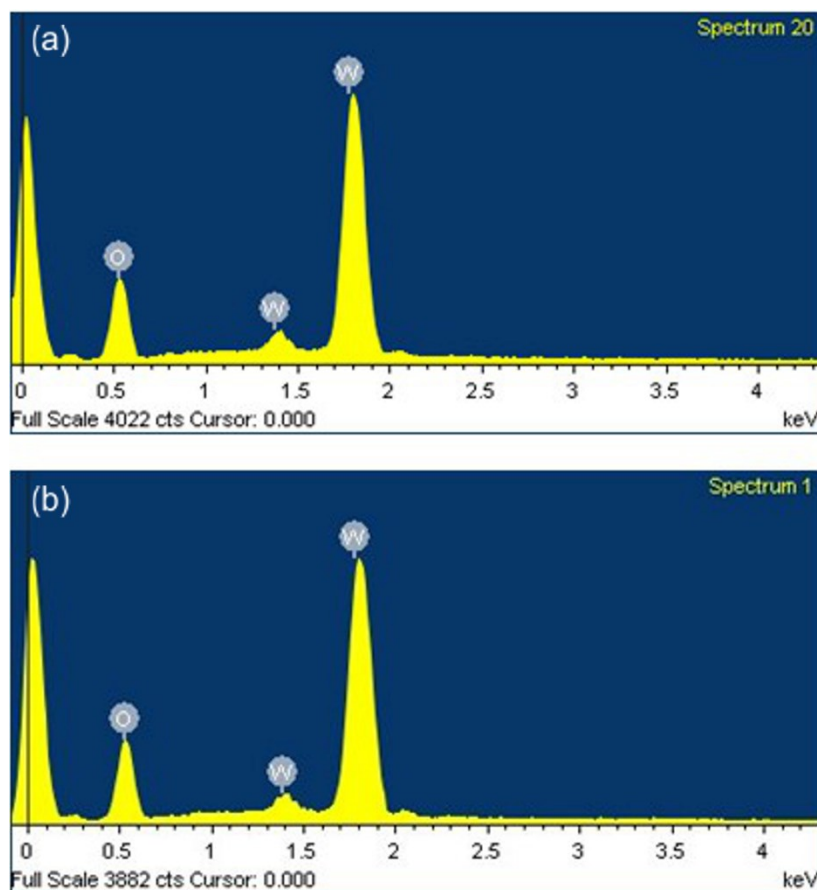


Fig. S2 EDX spectrum of the prepared materials: (a) WO₃-1; (b) WO₃-2. The EDX analysis of the samples were carried out on different areas of each material confirming the presence of expected W and O elements in the WO₃-1 and WO₃-2 structures.

Table S1 Table of the quantitative analysis of WO₃-1 and WO₃-2 materials obtained by EDX

Sample	W (Atomic%, ±2%)	O (Atomic%, ±2%)
WO ₃ -1	25.2	74.8
WO ₃ -2	25.6	74.4

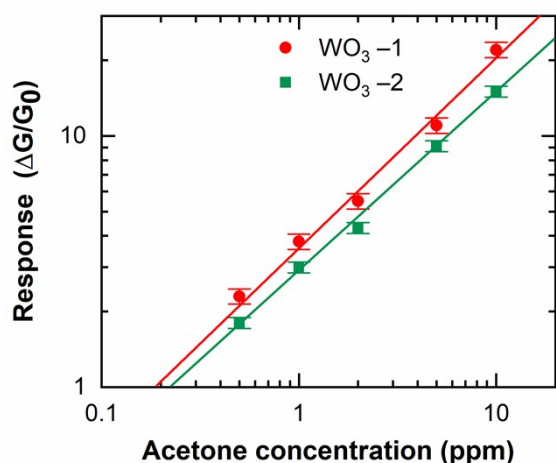


Fig. S3 Calibration curves of the normalized sensing response of WO₃-1 and WO₃-2 samples towards acetone at the operating temperature of 400 °C and RH of 40%. We set the response value ($\Delta G/G_0$) for both sensors to 1 to estimate their LOD. LODs for the WO₃-1 and WO₃-2 are about 170 and 220 ppb, respectively.

Table S2 Sensing parameters of WO₃-1 and WO₃-2 structures towards 500 ppb, 1, 2, 5 and 10 ppm of acetone at 400 °C of operating temperature and 40 % of RH. The response and recovery times of sensors were defined as the time to reach 90% of ΔG when the gas is introduced and to recover to 70% of the baseline conductance in air. The purging/filling time of the test chamber is about 300 s. Therefore, the lower values of response and recovery times registered by the gas test system can be varied depending on the measurement system and the volume of the test chamber.

Sample	Acetone concentration (ppm)	Response	Response time (s)	Recovery time (s)
WO ₃ -1	0.5	2.3	330	180
	1	3.8	180	180
	2	5.5	210	180
	5	11	180	150
	10	22	900	150
WO ₃ -2	0.5	1.8	420	180
	1	3	180	180
	2	4.3	300	180
	5	9.1	240	180
	10	15	950	150

Table S3 Dipole moments of the acetone and interfering gases

Gas	Dipole moment (D)
Acetone	2.88
Ethanol	1.69
NH ₃	1.47
Ethylene	0
CH ₄	0
CO ₂	0
CO	0.112

Table S4 Acetone sensing properties of different metal oxide nanostructures. R₀ and R_f are the resistance values of structures in air and in the presence of acetone, respectively. G₀ and G_f are the conductance values of structures in air and in the presence of acetone, respectively

Material	Concentration (ppm)	Responses	Operating temperature (°C)
WO ₃ nanofibers ¹	5	7.7 (R ₀ /R _f)	400
WO ₃ nanowires ²	200	1.4 (R ₀ /R _f)	300
Carbon-doped porous WO ₃ ³	10	13.5 (R ₀ /R _f)	390
polystyrene–WO ₃ nanofibers ¹	5	8.4 (R ₀ /R _f)	400
CeO ₂ –WO ₃ nanowires ⁴	0.5	1.3 (R ₀ /R _f)	250
Graphene oxide–WO ₃ nanofibers ⁵	100	35.9 (R ₀ /R _f)	375
Ag–WO ₃ nanosheets ⁶	100	12.5 (R ₀ /R _f)	340
Carbon-doped WO ₃ spheres ⁷	10	11.5 (R ₀ /R _f)	300
MO ₃ –WO ₃ ⁸	100	18.2 (R ₀ /R _f)	320
Cr ₂ O ₃ –WO ₃ nanowires ²	200	4.1 (R ₀ /R _f)	300
SnO ₂ spheres ⁹	5	6.6 (R ₀ /R _f)	400
ZnO–Fe ₃ O ₄ nanoparticles ¹⁰	50	47 (R ₀ /R _f)	485
WO ₃ –1 (This work)	0.5	2.5 (G _f /G ₀)	300
WO ₃ –1 (This work)	1	2.7 (G _f /G ₀)	300
WO ₃ –1 (This work)	5	7.8 (G _f /G ₀)	300
WO ₃ –1 (This work)	10	12.4 (G _f /G ₀)	300
WO ₃ –1 (This work)	0.5	3.3 (G _f /G ₀)	400
WO ₃ –1 (This work)	1	4.8 (G _f /G ₀)	400
WO ₃ –1 (This work)	5	12 (G _f /G ₀)	400

References

1. S.-J. Choi, S.-J. Kim, H.-J. Cho, J.-S. Jang, Y.-M. Lin, H. L. Tuller, G. C. Rutledge and I.-D. Kim, *Small*, 2016, **12**, 911–920.
2. S. Choi, M. Bonyani, G.-J. Sun, J. K. Lee, S. K. Hyun and C. Lee, *Applied Surface Science*, 2018, **432**, 241–249.
3. M.-D. Wang, Y.-Y. Li, B.-H. Yao, K. Zhai, Z.-J. Li and H.-C. Yao, *Sensors and Actuators B: Chemical*, 2019, **288**, 656–666.
4. K. Yuan, C.-Y. Wang, L.-Y. Zhu, Q. Cao, J.-H. Yang, X.-X. Li, W. Huang, Y.-Y. Wang, H.-L. Lu and D. W. Zhang, *ACS Applied Materials & Interfaces*, 2020, **12**, 14095–14104.
5. J. Zhang, H. Lu, C. Yan, Z. Yang, G. Zhu, J. Gao, F. Yin and C. Wang, *Sensors and Actuators B: Chemical*, 2018, **264**, 128–138.
6. M. Yin, L. Yu and S. Liu, *Materials Letters*, 2017, **186**, 66–69.
7. J.-Y. Shen, L. Zhang, J. Ren, J.-C. Wang, H.-C. Yao and Z.-J. Li, *Sensors and Actuators B: Chemical*, 2017, **239**, 597–607.
8. Y. Sun, L. Chen, Y. Wang, Z. Zhao, P. Li, W. Zhang, Y. Leprince-Wang and J. Hu, *Journal of Materials Science*, 2017, **52**, 1561–1572.
9. H.-J. Cho, S.-J. Choi, N.-H. Kim and I.-D. Kim, *Sensors and Actuators B: Chemical*, 2020, **304**, 127350.
10. L. Zhang, B. Dong, L. Xu, X. Zhang, J. Chen, X. Sun, H. Xu, T. Zhang, X. Bai, S. Zhang and H. Song, *Sensors and Actuators B: Chemical*, 2017, **252**, 367–374.