

W-Bi₂Sn₂O₇ Ultrafine Nanocrystals for Chemiresistive Monitoring of Volatile Organic Compound

Yiwen Zhou^{1,2,3}, Zichen Zheng^{1,2,3}, Xudong Nie^{1,2}, Ruiyu Hou^{1,2}, Carla Bittencourt³, Chao Zhang^{1,2}

¹ College of Mechanical Engineering, Yangzhou University, Yangzhou 225127, PR China,

² Jiangsu Key Laboratory of Surface Strengthening and Functional Manufacturing, Yangzhou University, Yangzhou 225127, PR China

³ Chimie des Interactions Plasma-Surface, University of Mons, 7000 Mons, Belgium

Corresponding Author's e-mail address: zhangc@yzu.edu.cn

Summary:

This work develops a high-sensitivity sensor based on tungsten-doped bismuth stannate (W-Bi₂Sn₂O₇) ultrafine nanocrystals for the detection of 4-ethylguaicol. The sensor demonstrates exceptional response to 4-ethylguaicol at trace concentrations of 2–10 ppm. The enhanced sensing performance is driven by electronic structure modulation and increased surface oxygen vacancies. This work underscores the potential of defect-engineered nanomaterials for advanced agricultural monitoring and real-time plant health diagnosis.

Keywords: gas sensor, room temperature, 4-ethylguaicol, metal oxide, doping

Background

Bismuth stannate (Bi₂Sn₂O₇), an n-type semiconductor characterized by its stable ilmenite-type lattice, holds immense promise for chemiresistive gas sensing due to its structural flexibility and, notably, its facilitated charge-transfer kinetics [1]. However, achieving high sensitivity at trace-level concentrations remains a formidable challenge for pristine Bi₂Sn₂O₇ [2]. Recent studies have demonstrated that the strategic incorporation of tungsten (W) into the metal oxide lattice has significant potential to modulate electronic properties and surface chemistry [3]. By employing a facile hydrothermal route to synthesize W-doped Bi₂Sn₂O₇ (W-Bi₂Sn₂O₇), this doping strategy synergistically induces the formation of abundant surface oxygen vacancies, creating high-density active sites for gas adsorption. Consequently, the sensor exhibits a superior, stable response to 2–10 ppm 4-ethylguaicol, enabling reliable trace detection.

4-Ethylguaicol is a volatile organic compound (VOC) released by plants as a defensive response to biotic or abiotic stressors, such as pathogen invasion or drought [4]. The emission intensity of 4-ethylguaicol correlates directly with the physiological health status of the crop, providing a real-time diagnostic signature for early plant stress detection. This work demonstrates the successful integration of W-Bi₂Sn₂O₇ ultrafine nanocrystals into gas sensing platforms, highlighting their potential as an indispensable

tool for precision agriculture and non-invasive plant health monitoring [5].

Sample preparation

A straightforward one-step hydrothermal method was used to synthesize tungsten-doped Bi₂Sn₂O₇. During the synthesis, tungsten hexachloride (WCl₆) was used as the dopant precursor, and the molar ratio of W to Bi was adjusted to approximately 0%, 2%, 4%, and 6%. The samples were designated as BSO, 2WBSO, 4WBSO, and 6WBSO, respectively. To evaluate the gas-sensing properties, a four-channel testing system was utilized to capture real-time resistance signals during cyclic exposure to ambient air and the target gases.

Results

Owing to its superior sensing metrics, the 4WBSO sample was selected as the representative sensor for in-depth structural analysis (Fig. 1). The morphological features of the synthesized QDs were examined via high-resolution transmission electron microscopy (HRTEM). As depicted in Fig. 1b, the 4WBSO exhibits an ultra-small grain size of 3–6 nm based on statistical analysis, consistent with the significant broadening observed in the XRD pattern (Fig. 1d), thereby enhancing surface reactivity. The corresponding selected area electron diffraction (SAED) pattern (Fig. 1d) illustrates the well-defined crystalline lattice of the doped stannate structure. Additionally, energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. 3e–3i)

highlights the homogeneous dispersion of Bi, Sn, O, and W atoms, confirming that tungsten has been successfully and uniformly incorporated into the $\text{Bi}_2\text{Sn}_2\text{O}_7$.

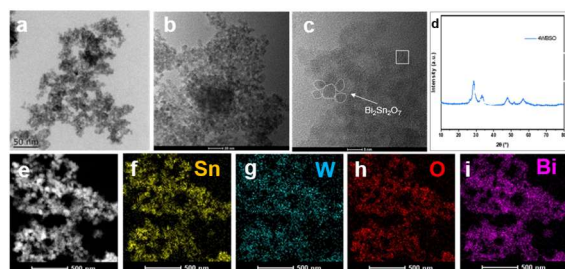


Fig. 1. (a) TEM images and (b-c) HRTEM image of 4WBSO, (d) XRD pattern of 4WBSO, (e) HAADF-STEM image of 4WBSO, (f-i) EDS elemental mapping images of Sn, W, O, and Bi for 4WBSO.

The O 1s spectra were deconvoluted into three Gaussian-Lorentzian components: lattice oxygen (O_L), chemisorbed oxygen (O_C), and oxygen vacancies (O_V). XPS O 1s analysis reveals that W-doping significantly increases the O_V relative concentration ($\text{O}_V/(\text{O}_C+\text{O}_L+\text{O}_V)$) from 24.4 % to 50.0 % (Table 1). A corresponding shift in binding energy from 529.7 eV to 530.3 eV confirms the strong electronic modulation by high-valence W^{6+} ions. These abundant O_V sites, combined with size effects, provide a high density of active centers, thereby facilitating enhanced adsorption of 4-ethylguaiaicol and superior sensing kinetics.

Tab. 1: Summary of O 1s Binding Energies and Relative concentration of Oxygen Vacancies (O_V) for BSO and 4WBSO Sample.

Sample	Binding Energy (eV)	$\text{O}_V/(\text{O}_L+\text{O}_C+\text{O}_V)$ (%)
BSO	529.7	24.4%
4WBSO	530.3	50.0%

Fig. 2 demonstrates that 4WBSO achieves the most significant response toward 4-ethylguaiaicol across the 2-10 ppm range at room temperature. The remarkable enhancement is primarily driven by the strategic incorporation of tungsten, which optimizes the amount O_V to a near-ideal level (approx. 50%), significantly modulating the electronic band structure and enhancing charge-carrier mobility. The high valence W^{6+} ions increase the number of chemisorption centers and introduce defect-induced energy levels. These states act as efficient electron traps, facilitating rapid charge transfer during interactions with 4-ethylguaiaicol molecules, thereby heightening sensitivity.

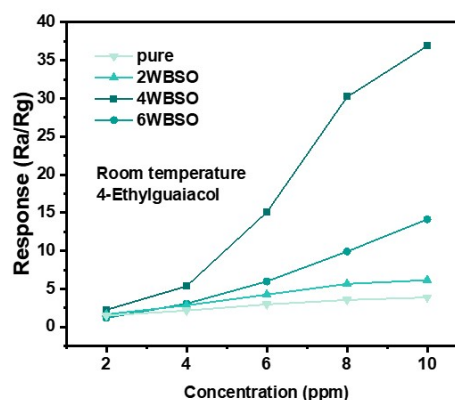


Fig. 2. The response values of WBSO ($x = 0, 2, 4$, and 5) film to 4-ethylguaiaicol (2-10 ppm) at room temperature.

Conclusion

W-doped $\text{Bi}_2\text{Sn}_2\text{O}_7$ ultrafine nanocrystals were successfully synthesized using a facile hydrothermal method. The optimized 4WBSO exhibits abundant oxygen vacancies and size effects. The developed sensor shows a superior response to 2-10 ppm 4-ethylguaiaicol at room temperature, providing a valuable tool for real-time plant stress monitoring.

References

- [1] T. Wang, W. Tao, X. Kou, L. Zhao, P. Sun, G. Lu, $\text{Bi}_2\text{Sn}_2\text{O}_7$ Overlayer Assists Bilayer Chemiresistor in Humidity-Independent and Highly Selective Detection of Expiratory Acetone, *ACS Sensors* 9, 6717–6727 (2024); doi: 10.1021/acssensors.4c02378
- [2] K. Liu, Z. Zheng, Y. Zhou, C. Bittencourt, M. Debliquy, Q. Liu, C. Zhang, Heterovalent-doping-induced ultrasensitive and highly exclusive ethylene sensor: Application to crop quality inspection, *Chemical Engineering Journal* 508, 161075 (2025); doi: 10.1016/j.cej.2025.161075
- [3] Z. Li, R. Paul, T. Ba Tis, A. C. Saville, J. C. Hansel, T. Yu, J. B. Ristaino, Q. Wei, Non-invasive plant disease diagnostics enabled by smartphone-based fingerprinting of leaf volatiles, *Nature Plants* 5, 856–866 (2019); doi: 10.1038/s41477-019-0476-y
- [4] Z. Li, Y. Liu, O. Hossain, R. Paul, S. Yao, S. Wu, J. B. Ristaino, Y. Zhu, Q. Wei, Real-time monitoring of plant stresses via chemiresistive profiling of leaf volatiles by a wearable sensor, *Matter* 4, 2553–2570 (2021); doi: 10.1016/j.matt.2021.06.009
- [5] A. Kumar, V. Krishnan, Vacancy Engineering in Semiconductor Photocatalysts: Implications in Hydrogen Evolution and Nitrogen Fixation Applications, *Advanced Functional Materials* 31, 2009807 (2021); doi: 10.1002/adfm.202009807M. Mouse, D. Duck, The Beagle Boys for President, *Journal of Applied Nonsense* 13, 123-134 (2011); doi: 10.1234/s10000