

Breath of Detection:
Advances in Tungsten Oxide Nanowire Gas Sensors

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ABSTRACT

Tungsten oxide nanowires have emerged as promising materials for gas sensing applications due to their one-dimensional structure, large surface-to-volume ratio, and tunable electronic properties. These nanostructures exhibit high sensitivity to various gases because surface interactions between adsorbed oxygen species and target molecules induce measurable changes in electrical resistance. This work reviews different techniques of synthesizing tungsten oxide nanowires, fundamental properties, including their composition, crystal structures, dimensionality, and surface chemistry, and discusses how these structural features influence sensing performance. The relationship between nanowire morphology, stoichiometry, and sensing behavior is examined, particularly the role of oxygen vacancies and surface defects in enhancing gas adsorption and charge transfer processes. Applications of tungsten oxide nanowires in detecting hazardous and environmentally relevant gases such as ammonia, hydrogen sulfide, and nitrogen dioxide are highlighted. Despite their advantages, challenges, including limited selectivity, high operating temperatures, and sensitivity to humidity, remain obstacles for practical deployment. Future research directions focusing on material modification, heterostructure engineering, and improved device integration are discussed to advance the development of high-performance gas sensors based on tungsten oxide nanowires.

1. INTRODUCTION

Various types of hazardous gases, including NO_2 , NH_3 , H_2S , H_2 , CH_4 , O_3 , CO_2 , acetone, and ethanol, are routinely released from industrial and agricultural processes or through daily-life activities.¹ If the concentration of these gases exceeds a critical threshold (sometimes as low as

parts per million, ppm), some of them, such as H_2 ² and CH_4 ,³ are highly explosive when exposed to air, whereas others, such as NO_2 ⁴ and NH_3 ,⁵ are harmful to human health and the environment. Therefore, the development of high-precision gas sensors is necessary.

The main function of a gas sensor is to detect the concentration and composition of a specific gas by converting a non-electrical signal into an electrical signal. Among all sensors, chemoresistive semiconductor gas sensors, in specific metal oxide semiconductor (MOS) material, stand out for their low cost, high sensitivity, fast response/recovery rates, good selectivity, low limit of detection (LOD), as well as the ability to detect a large number of gases.⁶ They have wide bandgaps, high dielectric constants, reactive electronic transitions, and good electrical, optical, and electrochromic properties, as well as superconductivity.⁷

Nanostructure materials are classified into three categories: zero-dimensional structures (e.g. quantum dots, nanoparticles, nanocrystals), one-dimensional (1D) nanostructures (e.g. nanowires [NW], nanorods [NR], nanotubes [NT]), and two-dimensional (2D) nanostructures (e.g. thin films), where the change in size and dimensionality will result in different structures and properties of the materials. Nanowires, 1D nanostructures, are characterized by a diameter of 1-100 nm but may have lengths of a few millimeters or more.⁷ Therefore, the 1D morphology is more suitable for the fabrication of building blocks, making electrical measurement with two terminals easier, which then holds a wide variety of applications, namely biosensors, smart windows, solar cells, light-emitting diodes, field emissions, and gas sensors, which will be discussed further.^{7,8}

In this paper, tungsten oxide nanowire is discussed for the application of gas sensors. In Section 2, we introduce some of the most common synthesis techniques for controllable morphology, identical shape, uniform size, and consistent chemical composition of 1D tungsten oxide nanowires. In Section 3, we discuss the relationship between nanostructure and properties

of the material, highlighting the unique characteristics for gas sensing. In Section 4, the application of gas sensors is acknowledged, and multiple gases that the material can detect are mentioned. Lastly, Section 5 contains concluding remarks and perspectives on 1D tungsten oxide nanowires. We hope this article can provide the readers with snapshots of the recent developments and future challenges of 1D nanowires.

2. SYNTHESIS METHODS

Tungsten oxide nanowires are composed of a network of WO_6 octahedra with shared oxygen at the corners. They can form not only stoichiometric WO_2 and WO_3 , but also non-stoichiometric WO_x ($2 < x < 3$), for example, $\text{W}_{18}\text{O}_{49}$ ($\text{WO}_{2.73}$), W_3O_8 , $\text{WO}_{2.9}$.⁷ Tungsten oxides have various crystalline phases, but this paper focuses on monoclinic and hexagonal phases. Their surface chemistry is dominated by oxygen vacancies, belonging to the n-type MOS, adsorbed oxygen or water molecules, and surface W–O or hydroxyl (–OH) groups, which strongly influence electrical conductivity, catalytic activity, and gas adsorption behavior. Thermal conditions play a key role in governing their structure: temperature controls phase transitions, defect formation, crystal growth mechanisms, and anisotropic heat transport, with heat and charge generally propagating along the nanowire axis due to their 1D geometry.⁸

A variety of synthesis techniques have been developed to synthesize 1D tungsten nanowires using liquid-/vapor-phase methods or nanostructure growth methods. In this paper, we present the most common synthetic methods and describe how they can be employed for engineering and tuning the morphology and properties of WO_x . because of its fascinating and promising functionalities, owing to its physical and chemical properties.

2.1. Solvent-based methods

Solvothermal and hydrothermal synthesis are widely used solution-based techniques for the fabrication of tungsten oxide (WO_x) nanostructures. Both methods involve chemical reactions in sealed vessels under elevated temperature and pressure, allowing controlled nucleation and growth of nanomaterials. The key difference between the two techniques lies in the solvent used: hydrothermal synthesis employs water as the reaction medium, whereas solvothermal synthesis utilizes non-aqueous organic solvents.^{9,16} These approaches provide excellent control over particle size, morphology, and crystalline phase, making them particularly suitable for the preparation of 1D WO_x nanostructures such as nanowires and nanorods.

2.1.1. Solvothermal method

Solvothermal synthesis is considered an effective technique for producing high-quality 1D nanostructures. In this method, reactions occur in a closed system at moderate to high temperatures (typically 100–1000 °C) and elevated pressures. Under these conditions, the solvent approaches its critical state, significantly increasing the solubility of many materials and enabling controlled crystal growth. In most solvothermal syntheses of nanostructured WO_x , tungsten hexachloride (WCl_6) is commonly used as the precursor. The precursor is dissolved in an organic solvent and transferred into a PTFE-lined autoclave (typically 120 mL). The sealed autoclave is then heated in a furnace at approximately 200 °C for 6–10 hours, depending on the experimental conditions. This process facilitates nucleation and subsequent growth of tungsten oxide crystallites. After the reaction, the resulting products are usually washed with ethanol before further characterization. Studies have shown that $\text{W}_{18}\text{O}_{49}$ nanowires synthesized through this method preferentially grow along the [010] crystallographic direction.^{9,10,11}

One of the most important factors affecting the solvothermal synthesis of tungsten oxide is the choice of solvent, which can significantly influence the stoichiometry, morphology, and crystalline phase of the resulting materials. For example, Choi et al. (2005) demonstrated that different solvent compositions produce different phases of tungsten oxide. Monoclinic $W_{18}O_{49}$ nanowires were synthesized in pure ethanol.⁹ Similarly, Sun et al. (2008) employed cyclohexane as the solvent and obtained bundled mixtures of $W_{18}O_{49}$ and WO_2 . They observed that increasing the concentration of WCl_6 led to larger, shorter, and straighter nanowire bundles, which eventually evolved into block-like structures.¹⁰ Further studies demonstrated additional control over nanowire morphology where monoclinic $W_{18}O_{49}$ nanowire bundles were synthesized, composed of ultrathin, parallel-aligned nanowires with diameters ranging from 2–15 nm using cyclohexane at relatively low temperatures.^{11,12} In another study, Qin et al. (2010) produced larger one-dimensional $W_{18}O_{49}$ bundles with diameters of 70–90 nm and lengths of 500–1000 nm using 0.01 M 1-propanol as the solvent.¹³

In addition to solvent control, dopant ions can be introduced to modify the growth kinetics and assembly of nanowires. It is reported that the incorporation of titanium ions promotes the secondary assembly of nanowires because titanium preferentially substitutes tungsten atoms due to its lower ionic valence.¹⁴ This substitution reduces the surface energy and leads to the formation of massive bundle structures with diameters reaching 400–500 nm. Beyond doping strategies, solvothermal synthesis can also be used to create heterostructured nanomaterials. For instance, Xiong et al. (2018) synthesized WO_3 - $W_{18}O_{49}$ heterostructures using isopropanol as a reducing agent. The resulting structures exhibited loose spindle-like morphologies composed of numerous well-aligned nanowires with diameters of 10–20 nm and lengths of 150–200 nm.¹⁵

2.1.2. Hydrothermal method

Hydrothermal synthesis is another widely used liquid-phase technique for producing tungsten oxide nanostructures with various morphologies. This method is relatively simple, cost-effective, and well-established for large-scale synthesis. In hydrothermal processes, reactions occur in aqueous solutions at elevated temperatures and pressures, enabling controlled crystal nucleation and growth. In most hydrothermal syntheses of WO_x nanostructures, tungstic acid (H_2WO_4) is used as the precursor. The precursor solution is sealed in an autoclave and maintained at temperatures typically between 120 and 300 °C for a specified period. Under these conditions, tungsten oxide nuclei form and grow into crystalline nanostructures.

Several studies have demonstrated that additives can significantly influence the morphology of hydrothermally synthesized tungsten oxide. For example, Gu et al. reported that alkali sulfates play an important role in controlling the morphology of hexagonal WO_3 (h- WO_3) nanowires. The addition of alkaline sulfates such as Na_2SO_4 , Li_2SO_4 , K_2SO_4 , and Rb_2SO_4 resulted in the formation of cylindrical bundles of uniform h- WO_3 nanowires.^{16,17,18}

Hydrothermal synthesis is also widely used to fabricate functional nanostructures for sensing applications. Yuan et al. synthesized CeO_2 -decorated WO_3 nanowires using a combination of hydrothermal treatment and thermal decomposition. These nanostructures were used as the active material in MEMS-based acetone gas sensors, and their structural and interfacial properties were verified using TEM, SEM, XPS, and XRD characterization techniques.¹⁹

More recently, an effective surface functionalization strategy has been demonstrated to improve both the sensitivity and long-term stability of WO_3 -based gas sensors. In the work, hexagonal WO_3 nanowires were modified with methylphosphonic acid (MPA) for ammonia (NH_3) detection. Fourier transform infrared spectroscopy (FTIR) and density functional theory (DFT)

calculations revealed that phosphate groups in MPA selectively bind to Lewis acid sites (under-coordinated W^{6+}) on the surface of h- WO_3 nanowires. This interaction effectively passivates the surface and suppresses degradation during sensing operation.²⁰

2.2. Thermal evaporation

Thermal evaporation deposition is a physical vapor deposition technique in which a source material is vaporized by heating, typically under vacuum or within a controlled, low-pressure gaseous environment. The generated vapor is then transported and condensed onto a cooler substrate, where it nucleates and grows into thin films or nanostructures.⁸ For the synthesis of tungsten oxide nanostructures, the source material is commonly tungsten metal (W) or WO_3 powder, which is heated to high temperatures that are still lower than its melting point (1470 °C). Figure 1 shows the schematic illustration of the thermal evaporation technique for growing WO_3 , where WO_3 powder is placed on top of the tungsten substrate inside the furnace and heated to ~1000 °C.

One of the early demonstrations of tungsten oxide nanowire growth by thermal evaporation was reported by Hong et al., who successfully synthesized $W_{18}O_{49}$ nanowires at relatively low temperatures without the use of catalysts. In their experiment, tungsten powder was placed in the high-temperature zone of a tube furnace at 650 °C, while a tungsten substrate was positioned in the low-temperature zone at 400 °C. This temperature gradient enabled the growth of $W_{18}O_{49}$ nanowires with diameters ranging from 10–50 nm and lengths of approximately 500–1500 nm. The resulting nanowires exhibited circular or polygonal cross-sectional shapes and were produced with high yield.²¹

In the same year, Baek et al. reported the synthesis of tungsten oxide nanowires through thermal evaporation of WO_3 powder at higher temperatures ranging from 900 to 1100 °C. Their

study revealed the formation of individual nanowires with diameters of about 70 nm, exhibiting clear lattice fringes with a spacing of 0.38 nm, corresponding to the (001) crystallographic planes of monoclinic WO_3 .²²

Later studies further investigated the crystalline phases produced by heating tungsten powder.²¹ Cao et al. reported the controlled synthesis of monoclinic WO_3 nanowire arrays on silicon substrates using a catalyst-free thermal evaporation process.²³ However, Nguyen et al. obtained results consistent with those of Hong et al. (2006), observing the formation of $\text{W}_{18}\text{O}_{49}$ nanowires under similar thermal evaporation conditions rather than monoclinic WO_3 .²⁴ This discrepancy suggests that factors such as growth temperature, oxygen concentration, and local reaction environment play critical roles in determining the final crystal phase of tungsten oxide nanowires.

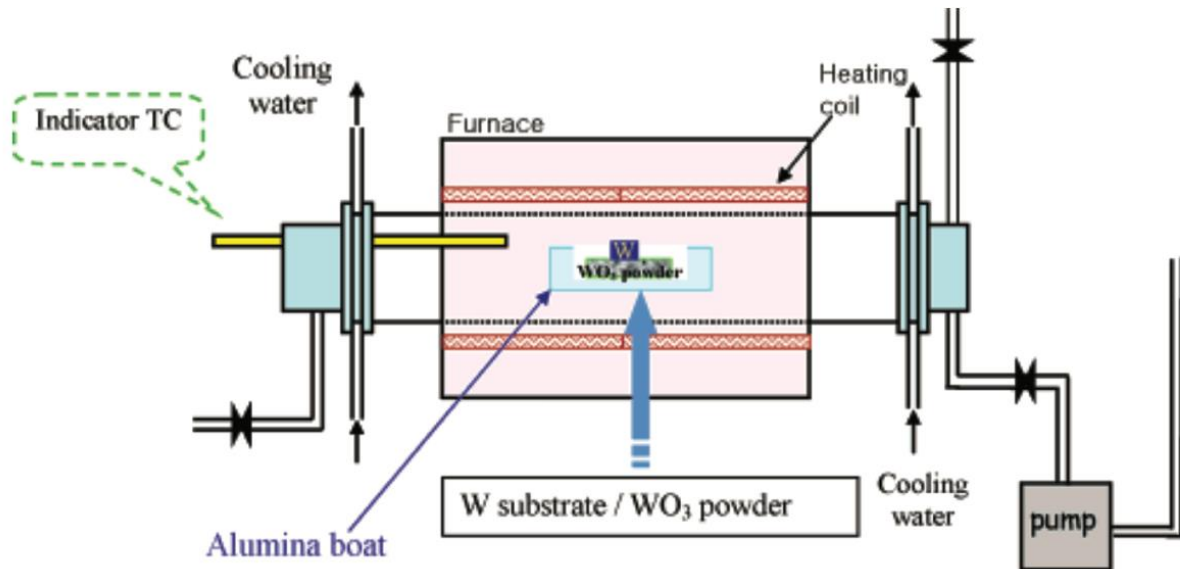


Figure 1. Schematic illustration of the furnace system used for WO_3 nanowire growth. Reproduced from Ref. 22.

2.3. Vapor-liquid-solid and Vapor-solid growths (VLS/VS)

The vapor-liquid-solid (VLS) growth mechanism is one of the most common techniques to synthesize nanowire structures. It was first reported for the growth of Si single crystals in 1964, and since then, it has been widely applied to other materials.²⁵ Metallic nanoparticles act as catalytic seeds that form a liquid eutectic alloy with the source material at elevated temperatures. A vapor-phase precursor supplies reactive species that dissolve into the liquid catalyst droplet, creating a supersaturated solution. Once supersaturation is reached, the dissolved material precipitates at the liquid–solid interface, forming a crystalline solid that grows downward as a one-dimensional nanowire while the catalyst particle remains at the tip. Continuous vapor supply maintains supersaturation, allowing the nanowire to elongate in a controlled manner along a preferred crystallographic direction (see Figure 2). In order to control the sizes and shapes of 1D nanostructures, the selection process of metals is the key.

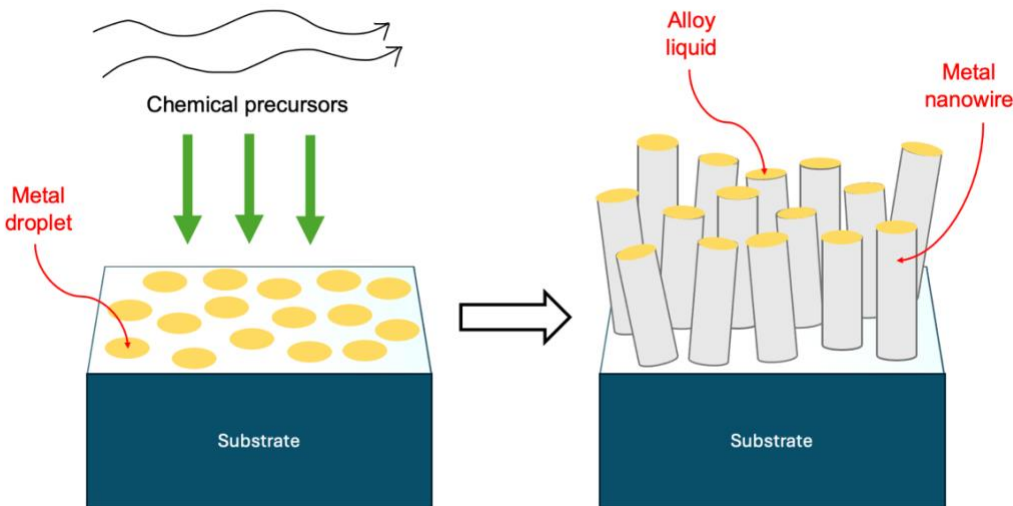


Figure 2. Schematic illustration of the vapor–liquid–solid (VLS) growth mechanism for tungsten oxide nanowires. (Self-produce)

In contrast, the vapor-solid (VS) growth is different from VLS growth since the mechanism requires no catalytic liquid metal to form a 1D nanowire. As based on the name, the process only has solid and vapor phases involved and self-catalysis as a main key point in high temperature conditions. The crystalline solids anisotropically gain material directly from the heavy active vapors along the preferential axis. During the heating process, tungsten oxide might be formed on the surface of the tungsten powders; the oxide was evaporated and redeposited on the substrate surface, forming 1D nanowires. Alternatively, the tungsten metal was vaporized first; a subsequent oxidation during the deposition on the substrate may also form the nanostructure.²⁶ It is reported that tungsten oxide nanowires can be synthesized by heating a tungsten wire partly wrapped with boron oxide powder (B_2O_3) in nitrogen atmosphere at $1600^\circ C$. The monoclinic WO_2 nanowires are 10–30 nm in diameter.²⁷

Tungsten oxide nanowires are more commonly synthesized through the VS mechanism than through the VLS growth mechanism for several reasons. First, VLS growth requires a liquid catalyst droplet, typically metals such as gold (Au), that can dissolve the source material and form a liquid alloy. However, tungsten has an extremely high melting point and very low solubility in common catalyst metals, making it difficult to form a stable liquid alloy droplet at typical growth temperatures. Another reason is that tungsten oxide readily forms volatile suboxide vapors during heating, which can directly condense into solid crystals on the substrate. This vapor-to-solid conversion naturally supports the VS growth pathway without the need for a catalyst. However, Kaur et al. were able to grow monoclinic WO_3 nanowire using the VLS method on the Au- and Pt-deposited alumina substrate with a diameter of 20-30 nm.²⁸

2.4. Characterization techniques

Common characterization techniques used to study tungsten oxide nanowires include methods for analyzing morphology, structure, composition, and sensing properties. Morphology is typically examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Crystal structure and phase identification are determined using X-ray diffraction (XRD) and selected area electron diffraction (SAED). Elemental composition can be analyzed using energy-dispersive X-ray spectroscopy (EDS). Surface chemical states are investigated using X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR), while Raman spectroscopy and UV–visible spectroscopy are used to study lattice vibrations and optical properties. In addition, theoretical calculations such as Density functional theory (DFT) are often employed to understand electronic structure, adsorption behavior, and gas–surface interactions. Electrical measurements are also conducted to evaluate gas sensing performance, including sensitivity, response time, and recovery behavior.

Table I. Synthesis methods for tungsten oxide nanowires

Materials	Crystalline structures	Material reactants	Methods	Temperature	Diameter (nm)	Note	Ref.
W ₁₈ O ₄₉	Monoclinic	WCl ₆	Solvothermal	200 °C – 5h	2-5	Ethanol	[11]
				200 °C – 10h	4-7		[9]
				200 °C – 24h	5-15		[12]
W ₁₈ O ₄₉	Monoclinic	WCl ₆	Solvothermal	200 °C – 9h	5-10	1-propanol	[7]
W ₁₈ O ₄₉ bundle	Monoclinic	WCl ₆	Solvothermal	200 °C – 6h	5-20	Ethanol	[4]
				200 °C – 9h	400-500	1-propanol Ti-added	[13]
W ₁₈ O ₄₉	Monoclinic	WO ₃ powder W substrates	Thermal evaporation	650 °C	10-50		[21]
		WO ₃ powder W foils		1000 °C	90-1000		[24]
WO ₃	Hexagonal	Na ₂ WO ₄ . 2H ₂ O	Hydrothermal	180 °C – 24h	10-15	K ₂ SO ₄ Citric acid	[16]
				180 °C – 24h	80	K ₂ SO ₄ Na ₂ SO ₄	[17]
				180 °C – 72h	5-25	Li ₂ SO ₄ Rb ₂ SO ₄	[18]
WO ₃	Monoclinic	WO ₃ powder W substrate	Thermal evaporation	900-1000 °C	70		[22]
		WO ₃ powder W substrate		1000 °C – 1h	40-100		[23]
WO ₃	Monoclinic	WO ₃ powder	VLS Growth	1100 °C	20-30	Au and Pt catalysts	[28]
WO ₂	Monoclinic	W wire	VS Growth	1600 °C	10-30	B ₂ O ₃ N ₂ atm	[27]
WO ₃ -W ₁₈ O ₄₉	Monoclinic	WCl ₆	Solvothermal	200 °C – 24	10-20	Isopropanol	[15]
CeO ₂ -decorated WO ₃	Monoclinic	Na ₂ WO ₄ . 2H ₂ O	Hydrothermal	200 °C – 8h	95		[19]
MPA@h-WO ₃	Hexagonal	WO ₃ powder	Hydrothermal	200 °C – 24h	20		[20]

3. PROPERTIES

This section focuses on the fundamental properties of nanostructured WO_x and starts with its various crystal structures and the conditions for phase transitions between these structures.

Tungsten oxide nanowires are one-dimensional nanostructured materials composed of tungsten and oxygen atoms arranged in a crystalline lattice. They belong to the class of transition-metal oxide semiconductors and are widely studied because their nanoscale geometry gives them a very high surface-to-volume ratio and unique electronic and optical properties. In terms of composition, tungsten oxide nanowires are primarily made of tungsten (W) and oxygen (O), most commonly in the form of tungsten trioxide (WO_3). However, the material often exists in slightly oxygen-deficient forms such as WO_{3-x} , where oxygen vacancies are present in the lattice. These vacancies play an important role in modifying the electronic structure and conductivity of the material, often enhancing its sensitivity in sensing or catalytic applications. The nanowire morphology means that the material is considered a 1D nanostructure, where the length of the structure is much greater than its diameter, allowing charge transport and other physical properties to be strongly influenced along the wire axis. Images a and b of Figure 3 demonstrate the structure of tungsten oxide nanowires through SEM images at different scales ($\text{W}_{18}\text{O}_{49}$ and WO_3), where they either have separated long, thin wires or bundles of thin wires. In addition, images c and d of Figure 3 clarify the identity of the nanostructure through XRD spectra through the indices.

The crystal structure of tungsten oxide can vary depending on temperature and synthesis conditions. WO_3 exhibits several polymorphs, including monoclinic, orthorhombic, tetragonal, and hexagonal phases. WO_3 crystals are generally formed by corner and edge sharing of WO_6 octahedra. At room temperature, monoclinic I (γ - WO_3) has been reported as the most stable

phase.¹⁵ However, in nanowire form, hexagonal structures are also frequently found because their open tunnel-like framework can facilitate nanowire growth during synthesis processes such as hydrothermal growth or vapor-phase deposition. However, this hexagonal crystal phase is metastable and reported to be transformed into a monoclinic structure when annealed at temperatures exceeding 400 ° C.¹⁰

WO₃ is a transition metal oxide made up of perovskite units, which is well-known for its nonstoichiometric properties, as the lattice can withstand a considerable amount of oxygen deficiency. Only a partial loss of the WO₃ oxygen content is needed to affect its electronic band structure and increase its conductivity by a large amount. However, the reduction of WO₃ is usually accompanied by structural changes. Some of the better-known nonstoichiometric WO_x compositions are W₂₀O₅₈, W₁₈O₄₉, and W₂₄O₆₈. For x values closer to 3, these shear planes are considered as extended defects if they are isolated or disordered. With further reduction in x, the shear planes tend to interact with each other and align in parallel, filling the space between the planes with corner-sharing WO₆. For x smaller than or equal to 2.87 (i.e., W₁₈O₄₉ and W₂₄O₆₈), the above-mentioned structures become unstable and further restructuring takes place involving the formation of pentagonal columns (PCs) parallel to the monoclinic b axis, which are either single or paired by edge-sharing (PC–PC).⁸

These structural factors ultimately determine application-specific properties. For example, in electrochromic devices, the crystal structure and stoichiometry influence ion diffusion and color-changing efficiency. For photocatalytic applications, the band structure and defect density affect light absorption and charge separation efficiency. And most importantly, the high surface area and abundant oxygen vacancies improve sensitivity in gas sensors because they facilitate adsorption and charge transfer with target molecules. Therefore, careful control of nanowire

structure, surface chemistry, and composition allows tungsten oxide nanowires to be optimized for different technological applications.

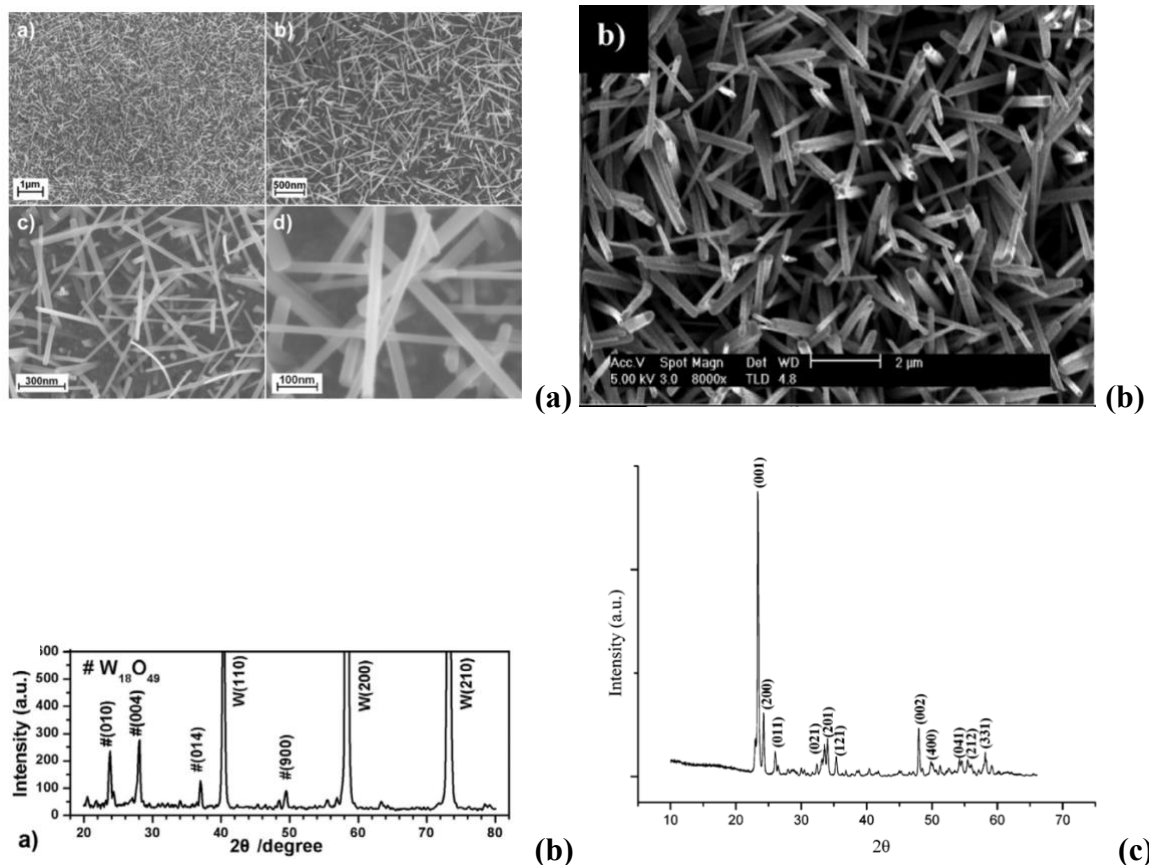


Figure 3. SEM images of tungsten oxide nanowires (a) W₁₈O₄₉ and (b) WO₃ at different magnifications and XRD spectrum of (c) W₁₈O₄₉ and (d) WO₃ nanowires. Reproduced from Ref. 21 and 22.

4. APPLICATIONS

Tungsten oxide nanowires are widely used in gas sensing applications because their 1D nanostructure provides a high surface-to-volume ratio and abundant active sites for gas adsorption. There are several gas sensing techniques, including Schottky Barrier or surface chemical reaction, but the oxygen adsorption/desorption model of chemiresistive mechanism (surface charge transfer) is used the most for tungsten oxide nanowire sensors.

4.1. Gas sensing mechanism

When WO_3 is exposed to air, due to the strong oxidation and electron affinity of oxygen, it forms a lower surface energy level. This causes oxygen molecules adsorbed on the surface of the sensitive layer to capture more electrons from the guide band of the WO_3 semiconductor, and the loss of electrons naturally leads to an electron depletion layer. At a certain temperature, the adsorbed oxygen can further evolve and form a lively ionic adsorbed oxygen species until the whole system reaches dynamic equilibrium. However, different operating temperatures, adsorbed oxygen exists in different forms, such as O_2^- , O^- , and O^{2-} .²⁹

When the n-type WO_3 semiconductor material is exposed to the target gas, the oxygen ions adsorbed on the surface of WO_3 will react with the target gas, causing the resistance of the material to change. When the target gas is a reducing gas, electrons are released back into the WO_3 body, reducing the resistance of the material and increasing the conductivity. In contrast, when the target gas is oxidizing, the WO_3 surface traps more electrons, and the resistance becomes larger. The gas sensor works by monitoring changes in the resistance of the sensitive layer material to determine the composition and concentration of the gas. Generally, the performance of gas sensors is evaluated by a number of important parameters, such as sensitivity, optimal operating temperature,

response/recovery time, selectivity/immunity, minimum detection limits, stability, and moisture resistance. Among them, the most critical parameter is sensitivity, the sensitivity based on the WO₃ gas sensor and can be summarized as:

$$S = R_a/R_g \text{ or } \Delta R/R_g \times 100\% \text{ (reducing gas)} \quad \text{Eq (1)}$$

$$S = R_g/R_a \text{ or } \Delta R/R_a \times 100\% \text{ (oxidizing gas)} \quad \text{Eq (2)}$$

where S stands for sensitivity, a is the resistance of the sensitive material stable in the air, and R_g is the resistance stable in the target gas.

Figure 4 shows the proposed illustrated mechanism of gas sensing of tungsten oxide nanowires with respect to H₂S and O₃ gases. The sketch predicts two different pathways for a gas to interact with the metal oxide surface, depending on its redox reaction structures. Overall, the detector uses the number of free electrons remaining in the material to signify the presence of one gas.

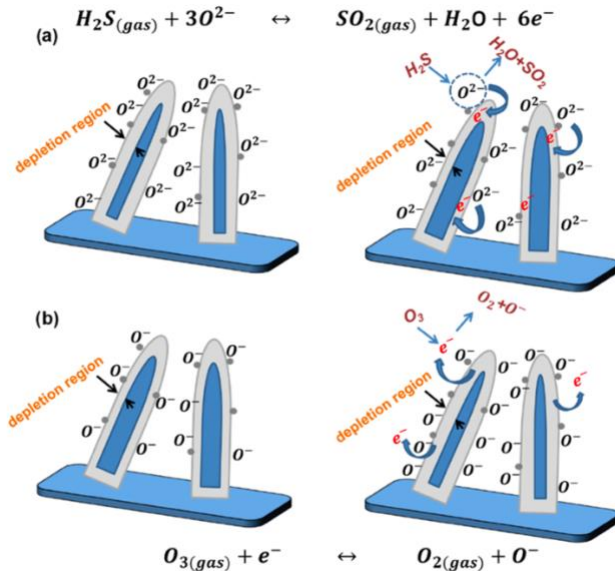


Figure 4. Sketch of the proposed gas sensing mechanism of the WO₃ nanowire sensor system toward (a) H₂S and (b) O₃. Reproduced from Ref. 28.

4.2. Detection of Various Gases with Emphasis on NO₂

Detecting nitrogen dioxide (NO₂) is important because it is a toxic air pollutant and a major contributor to environmental and health problems. Combustion processes, including vehicle exhaust, power plants, and industrial activities, primarily produce NO₂. Since it can leak during storage, transportation, or industrial processes, reliable gas sensors are needed to monitor its concentration and ensure safe working conditions.

Gas-sensing tests revealed that the sensor based on the WO₃ nanowire array could detect NO₂ concentrations as low as 50 ppb, demonstrating promising potential for low-concentration gas detection.²³ This data shows better results as compared to the WO₃ nanowire bundle-like structure, as the sensor can detect NO₂ gas at a concentration down to 0.25 ppm for operating temperatures ranging from 200 °C to 350 °C.²⁴ The sensor showed an immediate response to NO₂: the typical response times are less than 30 s; however, it took a relatively long time for the sensor recovery, generally more than 800 s, and it increased as the exposure concentration increased.^{23,24} Nguyen et al. were able to report that WO₃ synthesized at 1050 °C formed bundles and porous NWs that exhibited the highest response to NO₂ gas compared with that at 950 or 1000 °C (see Figure 5).²⁴

The nonstoichiometric crystalline structures of W₁₈O₄₉ may exhibit better gas-sensing performance compared with fully oxidized WO₃ materials, but they can convert to WO₃ at elevated temperatures.²⁴ This hypothesis was proven as W₁₈O₄₉ shows their high response value for low concentration exposure of NO₂ gas, which shows better performance than WO₃ nanosheet (see Figure 6).¹³ However, the response and recovery time of W₁₈O₄₉ is still an issue since they take so long to detect (100-200 s), and as the temperature rises, the time taken reduces significantly.^{13,24} To maximize the ability to detect NO₂ of W₁₈O₄₉, the tungsten oxide nanostructures were modified

with a Ti additive. The response times varied in the range of 1–50 s to 0.2–4 ppm NO₂ gas.¹⁴ These results indicate that the tungsten oxide nanowire is a promising gas-sensing material for a high-performance NO₂ gas sensor.

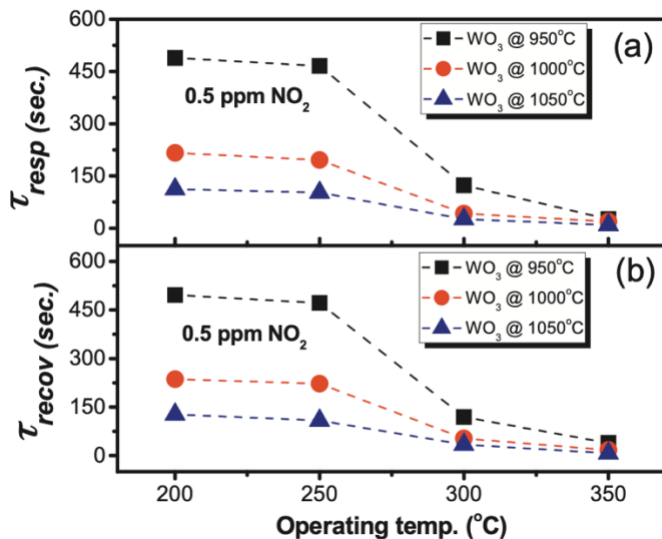


Figure 5. Response (a) and recovery (b) times of the WO₃ NW sensors synthesized at 950, 1000, and 1050 °C as a function of operating temperatures to NO₂ gas. Reproduced from Ref. 19.

Beyond nitrogen dioxide detection, tungsten oxide nanowires have demonstrated sensing capability toward a wide range of gases. These include oxidizing gases such as ammonia (NH₃), hydrogen sulfide (H₂S), and ozone (O₃),²⁸ as well as reducing gases including hydrogen (H₂).¹⁵ In addition, they have shown sensitivity to greenhouse and combustible gases such as carbon dioxide (CO₂) and methane (CH₄),¹⁵ along with volatile organic compounds including ethanol^{15,16} and acetone.^{16,18} The sensing performance arises from the interaction between these gas molecules and the chemisorbed oxygen species on the surface of tungsten oxide nanowires, which induces charge transfer and modifies the electrical conductivity of the material. This broad sensitivity highlights the versatility of tungsten oxide nanowires as promising materials for environmental monitoring, industrial safety, and air-quality sensing applications.

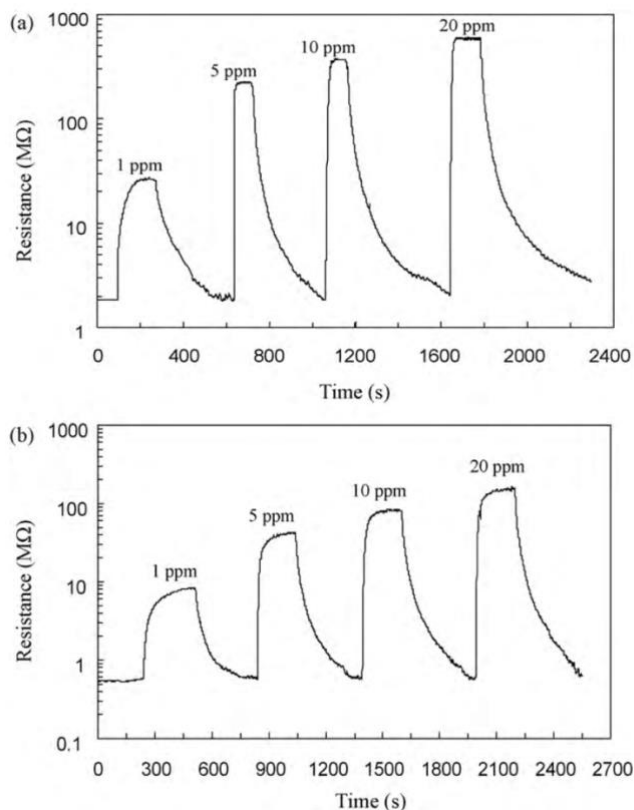


Figure 6. Dynamic response of (a) bundled $W_{18}O_{49}$ nanowires, (b) WO_3 nanosheets to varying NO_2 concentration at an operating temperature of $200\text{ }^\circ\text{C}$. Reproduced from Ref. 13.

4.3. Challenges and limitations

Although having the promising performance of gas sensing applications, tungsten oxide nanowires still have some remaining challenges that hinder them from widespread practical uses. One major limitation is poor selectivity. The material often responds to multiple gases because of its high detection ability, but that also creates another challenge of mixed signals and distinguishing difficulties without additional filtering. Another challenge is the high operating temperature for the metal oxide gas sensors. As discussed, in many cases, tungsten oxide nanowire sensors show optimal detection ability at temperatures above $400\text{ }^\circ\text{C}$ to activate surface reactions between adsorbed oxygen species and target gas molecules. Furthermore, $W_{18}O_{49}$ nanowires are

found to exhibit various crystalline defects such as stacking faults, dislocations, and oxygen vacancies after thermal treatment at 400-450 °C.³⁰ This behaviour highlights the importance of studying more of the reproducibility and stability of tungsten oxide nanowires with respect to temperature and humidity. Finally, the issue of response and recovery time should be further investigated since it was reported to be quite slow as compared to other gas sensing mechanisms. Integrating nanowires into reliable sensor devices with stable electrical contacts and scalable fabrication methods also remains an important area of ongoing research.

5. OUTLOOK

In summary, tungsten oxide nanowires have attracted significant attention as promising materials for gas sensing due to their one-dimensional nanostructure, high surface-to-volume ratio, and tunable surface chemistry. Their semiconducting properties allow sensitive detection of various gases through changes in electrical resistance caused by surface charge transfer and reactions with adsorbed oxygen species. As discussed, tungsten oxide nanowire sensors have demonstrated strong responses toward several hazardous and environmentally relevant gases, including ammonia, hydrogen sulfide, and nitrogen dioxide, as well as other gases and volatile organic compounds. These sensing capabilities highlight their potential applications in environmental monitoring, industrial safety, and air-quality control. Looking forward, future studies may focus on strategies such as noble metal decoration, heterostructure formation, and surface functionalization to enhance selectivity and sensitivity. With continued progress in nanomaterial synthesis and device engineering, tungsten oxide nanowires are expected to play an increasingly important role in next-generation gas sensing technologies.

6. REFERENCES

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