Metal–Oxide Nanowire Molecular Sensors and Their Promises

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Abstract: During the past two decades, one-dimensional (1D) metal–oxide nanowire (NW)-based molecular sensors have been witnessed as promising candidates to electrically detect volatile organic compounds (VOCs) due to their high surface to volume ratio, single crystallinity, and well-defined crystal orientations. Furthermore, these unique physical/chemical features allow the integrated sensor electronics to work with a long-term stability, ultra-low power consumption, and miniature device size, which promote the fast development of “trillion sensor electronics” for Internet of things (IoT) applications. This review gives a comprehensive overview of the recent studies and achievements in 1D metal–oxide nanowire synthesis, sensor device fabrication, sensing material functionalization, and sensing mechanisms. In addition, some critical issues that impede the practical application of the 1D metal–oxide nanowire-based sensor electronics, including selectivity, long-term stability, and low power consumption, will be highlighted. Finally, we give a prospective account of the remaining issues toward the laboratory-to-market transformation of the 1D nanostructure-based sensor electronics.

Keywords: nanowire; oxide; gas sensor; device; 1D nanostructure; sensing mechanism

1. Introduction

For the upcoming “trillion sensor electronics” era, molecular sensor and electronic recognition devices, which collect the enormous chemical information as big data from various volatile organic molecules (VOCs), are gaining increasing interests in health care [1–3], environment [1,4,5], security [6–9] and agriculture areas [3,4,10,11]. Among various molecular sensors, chemiresistive sensors integrated with metal–oxide semiconductor (MOS) nanostructures are of particular interest due to their high sensitivity and fast response [12–16]. Especially with the advancement of nanomaterial fabrication technology, a large number of functional MOS nanostructures, such as nanodots [17,18], nanowires [19–22], nanosheets [23–25], and hierarchical nanostructures [26–28], are synthesized as building blocks for the fabrication of sensor electronics.

Among these nanostructured forms, 1D MOS nanowires offer an ideal platform for nanoscale sensor integration due to their high surface to volume ratio, comparable sized Debye length, high crystallinity, excellent surface chemical reaction, and low power consumption [29–31]. Ever since the first report of using the 1D metal–oxide nanowire as the gas sensor by Comini, great progress has been achieved in the past two decades [32]. To date, hundreds of papers have been published on molecular sensors integration based on 1D metal–oxide nanostructures (SnO2 [29], In2O3 [33], Fe2O3 [34], V2O5 [35], CeO2 [36], ZnO [37], WO3 [38], NiO [39], CuO [40], NaNbO3 [41], Zn2SnO4 [42,43], CdIn2O4 [44], etc.), and the numbers of publications related to nanowires and metal–oxide nanowire sensors can be seen in Figure 1. Meanwhile, to fulfill multiple demands of molecule detection...
and monitoring, nanowire-based sensor devices with different structures, such as flat [45], suspended [46], bridging [47], and vertical structure [48], have also been addressed. Despite much effort being devoted to advancing the metal–oxide nanowire-based molecular sensor electronics, molecular sensors based on 1D MOS nanowires have not yet been successfully commercialized compared to the MOS film structures.

Figure 1. Numbers of publications in the area of nanowires and nanowire sensors from 1997 to 2021 (internet search of the Web of Science on 15 January 2021). Keywords for search: metal–oxide nanowire; metal–oxide nanowire + gas/molecular sensor.

The inherent limitations for the practical applications of the 1D MOS nanowire-based molecular sensors can be summarized as follows:

(1) Lack of effective method for the large-scale synthesis of geometrically uniform single-crystalline nanowires—as is known, the electrical [49], optical [50], thermal [51], and chemical [52] properties of nanomaterials are strongly affected by their size and shape due to the quantum confinement effect [53]. The electrical conduction becomes more sensitive to the field-effect as the nanowire diameter decreases [54]. Until now, although highly crystalline MOS nanowire with various diameters [55], compositions [28–40] and heterostructures [56,57] can be grown in vapor phase (physical vapor deposition (PVD) [58,59], pulsed laser ablation deposition (PLD) [60,61] and chemical vapor deposition (CVD) [62,63], etc.) and solution phase (hydrothermal [64,65] and solvothermal [66,67]), the large-scale synthesis of geometry uniform (diameter) nanowires is still a big challenge [68].

(2) Poor reproducibility—it has been demonstrated that the nanowires present a fantastic performance as they are integrated into single nanowire devices [69]. For such a kind of device, lithography and sputtering techniques are frequently utilized to design and deposit interdigitated electrodes on randomly distributed nanowires for the device fabrication [70]. However, this process is only accessible for fundamental laboratory research, and assembling scalable and controllable nanowires on arbitrary substrates remain a major challenge toward performance reproducible sensor device fabrication [71].

(3) Poor environmental/thermal stability—to deeply exploit the data science from the obtained sensor signal, the long-term stability of the sensor response is highly required for time-series data collection [72]. However, performance degradation usually occurs in the nanowire-based sensor electronics because the surrounding oxygen, water, and contaminants would react with the active nanowire surface as well as the nanowire–electrode contact when the sensors are exposed to ambient air for molecular detection [47,73,74].

(4) Poor sensor selectivity—although the sensitivity of the single nanowire sensor devices has been demonstrated to possess an exponential enhancement as compared with those thin-film devices [75,76], it is still desired to significantly improve the selectivity of nanowire-based sensor electronics. Therefore, further efforts are still encouraged to promote MOS nanowire-based sensor electronics for the IoT applications.
Here, in this review, we first give a comprehensive overview of the recent studies and achievements in 1D MOS nanowire synthesis, sensor device fabrication, device functionalization, and sensing mechanisms. Then, some critical issues that impede the practical application of the 1D MOS nanowire-based sensor electronics, including selectivity, long-term stability, and low power consumption, will be pointed out. Finally, we give an outlook of the remaining issues towards the lab-to-market transfer of the 1D nanostructure-based sensor electronics.

2. Metal–oxide Nanowires Growth

Nanowire-based electronics offers an excellent possibility for future systems beyond the limitation of Moore’s law and provides a promising platform to explore the physical origin and intrinsic properties. In recent decades, significant efforts and progress have been made, and many methods have been developed to synthesize 1D metal–oxide nanowires, including PVD, CVD, PLD, thermal oxidation and solution-based growth for single-crystalline nanowires, and template growth, electro-spun for polycrystalline/amorphous nanowires. Here, this section will mainly focus on the metal–oxide nanowires growth mechanism.

2.1. Vapor–Liquid–Solid Growth (VLS Growth)

The vapor–liquid–solid (VLS) mechanism is widely employed to grow high-quality nanowires [77–89]. In a typical VLS growth, as shown in Figure 2, a metallic catalyst droplet is firstly formed via heating the pre-deposited metal catalyst thin film. Then, by continuously feeding the vapor species to the metallic catalyst at an elevated temperature, a liquid eutectic alloy is formed. Finally, once the alloy reaches super-saturation, nanowires can be anisotropically grown from the nucleated seeds at the liquid–solid interface and the length of nanowires can be controlled by the growth time.

![Figure 2. A typical vapor-liquid-solid (VLS) growth mechanism in metal–oxide nanowire fabrication.](image-url)

In 1998, the Lieber group firstly reported a laser ablation technique for gaining VLS silicon nanowires [81]. Following this interesting work, various methods such as CVD, PVD, PLD, electron beam evaporation, and molecular beam epitaxy (MBE) have been developed to grow the metal–oxide nanowires ITO [90–92], NiO [93–95], ZnO [83,96], SnO₂ [97,98], TiO₂ [99,100], In₂O₃ [101,102], MgO [103–105], etc. [106,107].

In recent years, the Yanagida Lab (The University of Tokyo) has made great efforts in the VLS growth of metal–oxide nanowires [85,86,98,99,105,108–131]. They have pointed out that materials flux is an important variable which has been underestimated in VLS nanowires growth. For example, via precisely controlling the material flux within an order of magnitude, the structure and composition of VLS growth ITO nanowires can be altered from Rutile structure (Sn 100%, In 0%) to Fluorite structure (Sn 28%, In 72%) and Bixbyite structure (Sn 21%, In 79%) [86]. Moreover, the proposed “material flux window” concept from their group has been successfully applied for the synthesis of SnO₂, In₂O₃, ITO, ZnO,
NiO, MnO, CaO, Sm₂O₃, Eu₂O₃ and MgO nanowires [85]. Nevertheless, the VLS process of metal–oxides growth generally requires relatively high temperatures (600–1000 °C), which essentially limits their practical applications.

To solve this problem, Zhu et al. demonstrated a rational method to reduce the growth temperature via using the concept of “materials flux window” [83]. As shown in Figure 3a, it was found that a reduction in growth temperature can be successfully achieved via precisely controlling the vapor flux which originates from the suppression of nucleation at the vapor–solid interface. By optimizing an appropriate vapor flux for VLS nanowire, this concept can be applied to reduce the growth temperature for various metal–oxides, including ZnO (from 750 to 400 °C), SnO₂ (from 750 to 400 °C), and MgO (from 800 to 350 °C), as shown in Figure 3b–d. In addition, it has shown a successful application of this concept for the VLS growth SnO₂ nanowire on tin-doped indium oxide (ITO) glass at 500 °C and ZnO nanowires on polyimide (PI) substrates at 350 °C.

![Figure 3](image_url)

**Figure 3.** (a) The concept of “materials flux window” for nanowire growth (VLS, Vapor–Liquid–Solid; VS, Vapor–Solid); SEM image of (b) SnO₂ nanowires; (c) ZnO nanowires; and (d) MgO nanowires fabricated under the guidance of ‘materials flux window’. Reprinted from reference [83] with permission from the American Chemical Society.

### 2.2. Vapor–Solid Growth (VS Growth)

In the absence of a metal catalyst, 1D material structures can also be directly formed from the vapor phase into the solid phase, that is, the VS growth (Figure 4). In the view of the current studies, VS growth mechanisms are generally concluded as three types: (1) The anisotropic growth mechanism: nanowires can be synthesized via the preferential reactivity and binding of gas reactants on a specific surface to minimize the total surface energy [132–134]; (2) The defect-induced growth (or screw dislocations) mechanism: the growth of crystal proceeds by adding atoms at the kink sites of a surface step [135–139]; (3) The self-catalytic growth mechanism: metal–oxide can be decomposed into metal and oxygen by heating under vacuum condition, then the metal vapors are condensed and forming liquid droplets on a lower temperature substrate, and such droplets are the ideal catalysts for metal–oxide nanowire growth [140–151]. Similar to VLS growth, various metal–oxide nanowires, such as Ga₂O₃, ZnO, MgO, Ir₂O₃, and SnO₂ [140–153], have been successfully synthesized via VS growth. Furthermore, by using surface-roughness-assisted or seed-layer-assisted VS growth, nanowires can be also grown in a selective area [154–156].
Compared with VLS growth, VS growth nanowires are suffering from insufficient ability to control uniformity, which usually results in a tapered morphology of nanowires. Recently, Anzai et al. reported a negative effect of VS growth on the tapered SnO$_2$ nanowire electrical performance [79]. By using spatially resolved single nanowire electrical measurements, plane-view electron energy-loss spectroscopy and molecular dynamics simulations, it has been observed that the VS growth will generate a large number of defects in the oxides, thus making an unintentional doping in the nanowire structure. As shown in Figure 5d, such an unintentionally doping effect will cause a seven orders increase in the conductance, which entirely alters the intrinsic properties of nanowires. Furthermore, in light of their latest results, oxygen deficiency is the critical factor of the unintentionally doping effect in the VS growth [157]. Moreover, increasing oxygen partial pressure during the VS growth is an alternative way to prevent this drawback.

Figure 4. A typical Vapor–Solid (VS) growth mechanism in nanowire fabrication.

Figure 5. Anomalous electrical properties of VS growth nanowire: (a) a schematic image of unintentional carrier doping occurs at the vapor–solid interface during VS growth; (b) single tapered VS+VLS growth SnO$_2$ nanowire device; (c) single untapered VLS growth SnO$_2$ nanowire device; (d) IV curves of VS growth (93.0 kΩ) and VLS growth nanowire (2.04 TΩ); Reprinted from reference [79] with permission from the American Chemical Society.
2.3. Solution Phase Growth

The solution-phase growth, for example, the hydrothermal growth, is extensively used for the synthesis of metal–oxide nanowires [64,65,158–160]. Compared with the vapor phase growth (both VLS and VS), a much lower temperature is required for the solution growth, which allows the nanowires to be directly integrated on the flexible organic substrates for the modern wearable device. In addition, the morphology and properties of the solution phase growth nanowires can be conveniently manipulated by tuning the concentration of the composition, introducing additional composition, or adding additives in the solvent.

In the case of ZnO nanowires, the concept of a “concentration window” in the control of ZnO nanowire morphology has been demonstrated by He et al., as shown in Figure 6a [111]. Via carefully controlling the concentration of Zn ionic species within a specific concentration range, a selective growth on the (0001) plane can be realized. Meanwhile, under the guidance of a “concentration window”, Sakai et al. achieved a significant improvement in the growth rate of ZnO nanowires (up to 2000 nm/h) with the assistance of ammonia, as shown in Figure 6b [161]. Moreover, Joo et al. pointed out that the axial and radial growth of ZnO nanowire can also be controlled by introducing and tuning the amount of Cd (Cu, Mg, Ca) ions or Al (In, Ga) ions in the growth solution, respectively [161]. Not only in the growth of ZnO nanowires, other anisotropic 1D nanowires can also be controlled via tuning the concentration of additives. For example, Choi et al. reported a straightforward process for synthesizing tungsten oxide nanostructure with various morphologies [162]. By changing the composition of the solvent, the crystalline phase of tungsten oxide, such as mono-clinic W_{18}O_{49} nanowires (with ethanol), hexagonal WO_{3} platelets (with water/ethanol ratio (1:9)), and monoclinic WO_{3} nanosheets (with water) can be alternatively controlled. Currently, many kinds of nanowires, such as SnO_{2}, ZnO, TiO_{2}, In_{2}O_{3}, MnO_{2}, and WO_{3}, have been successfully synthesized via solution-phase growth with/without the assistance of the seed layer [160,163–173]. Owing to the low cost, less hazardous, no metal catalysts, the effectively controllable morphology and properties, the solution phase growth strategy has been successfully integrated into a well-developed micro-electro-mechanical system (MEMS) [174–176].

![Figure 6.](image-url) Face-selective control of hydrothermal zinc oxide nanowire: (a) schematic of a concentration dependence on the crystal growth of hydrothermal ZnO nanowires as a crystal-plane dependence on a critical nucleation concentration. Reprinted from reference [111] with permission from the American Chemical Society; (b) Zn concentration dependence of ZnO nanowire morphology with HMTA 15 mM with ammonia addition 500 mM. The Zn concentration range, where a nanowire can be grown, is highlighted by a red color. Reprinted from reference [161] with permission from the Nature Publishing Group.

2.4. Thermal Oxidation Growth

The thermal oxidation method is an easy way to massively grow metal–oxide nanowires in situ [177]. For example, Sn and Ga oxide nanowires can be easily obtained as the environment temperature increases over their melting points in the air or water vapor surroundings [31,178]. Interestingly, Zn, W, Fe, Mo, and Cu oxide nanowires can be grown
by the thermal oxidation method at an even lower temperature [179–187]. As shown in Figure 7a–c, several possible mechanisms have been invoked to account for the thermal oxidation growth: (1) Evaporation and condensation [179,188]; (2) Fast internal diffusion along a tunnel centered on the core of a screw dislocation [180,189]; (3) Surface diffusion along the sides of nanowires [181,190]. For example, α-Fe₂O₃ nanowires are spontaneously grown due to the fact Fe ions tend to leave from the compressed regions at the Fe₂O₃/Fe₃O₄ interface and diffuse to the stress-free Fe₂O₃ surface layer, whereas CuO nanowires are basically grown due to the continuous diffusion of Cu ions from the substrate to the tip of nanowires through the internal grain boundary, as depicted in Figure 7d,e [181,189].

![Figure 7](image-url)

**Figure 7.** The various mechanisms proposed for metal–oxide nanowire (NW) growth during the oxidation of metal: (a) evaporation and condensation; (b) internal diffusion along with the core of a screw dislocation; (c) surface diffusion along the sidewall of nanowires; (d) Fe₂O₃ nanowire growth following the surface diffusion mechanism. Reprinted with permission from Reference [181] Copyright 2012 Elsevier; (e) CuO nanowire growth follows the internal diffusion mechanism. Reprinted with permission from Reference [189] Copyright 2011 Elsevier; and (f) CuO nanowire device fabricated by thermal oxidation method. Reprinted with permission from Reference [177] Copyright 2012 Elsevier.

Owing to the in situ growth behavior of nanowires, a novel and simple technology has been reported by Steinhauser et al. for the fabrication of CuO nanowire sensors [177]. Via heating the Cu layer loaded on the patterned electrodes in air, CuO nanowires were naturally grown from the electrodes. By increasing the growth time, nanowires on foreign electrodes were mutually attached, forming the nanowire–nanowire conductive junctions as a functional sensing channel. Due to its simplicity and lack of post-processing steps after nanowire synthesis, this technique has been extensively employed to integrate CuO nanowires in a sensing device [191–193].

### 2.5. Template-Assisted Growth

Metal–oxide nanowires can be achieved by merely depositing oxide materials into an organic template such as poly(methyl methacrylate) (PMMA) or an inorganic template such as anodic aluminum oxide (AAO). The diameter, density, and length of the nanowires can be conveniently controlled based on the template design, as shown in Figure 8. Kolmakov et al. has shown a typical inorganic template-assisted growth method to synthesize SnO₂ nanowires [29]. By depositing Sn into nanoporous alumina and further etching the template by NaOH solution (or cracking by sonication), highly crystalline Sn nanowires
are harvested. Then, via processing an air annealing on the metallic Sn nanowires, SnO₂ nanowires are obtained.

Ra et al. reported the use of an organic template for obtaining ZnO nanowires [194]. As depicted in Figure 9, a-carbon was first deposited on the SiO₂/Si wafer as an etch-stop layer. Then, the wafer was coated by a sacrificial layer via plasma-enhanced chemical vapor deposition (PECVD). Then, the PECVD layer was patterned using conventional lithography and etched by the CF₄/Ar inductively coupled plasma (ICP) process. Then, an atomic layer deposition (ALD) process was used to create a 70 nm ZnO layer over the pre-patterned sacrificial layer. Then, by ICP etching with Cl₂/Ar discharges, the ZnO layer was removed except for the spacer part. Finally, ZnO nanowire arrays were obtained by removing the sacrificial oxide layer. A similar fabrication process for CuO, NiO, and Cr₂O₃ nanowires has also been recently reported [195]. Such patterning methods by using lithography techniques can prevent the problems associated with the alignment of the nanowires.

2.6. Electro-Spun Growth

Electro-spinning is one of the easiest, template-free, versatile, and cost-effective approaches to produce 1D nanostructures. Almost all the oxides and mixed oxides nanowires can be fabricated using this method [196–210]. Figure 10 shows a typical example of nanowires/nanofibers fabrication by electro-spun growth [201]. As shown in Figure 10a, an appropriate ratio of dimethylformamide, poly(vinyl acetate) (PVA), titanium(IV) propox-
Electro-spinning is one of the easiest, temperature-free, versatile, and cost-effective approaches to produce 1D nanostructures. Almost all the oxides and mixed oxides nanofilms can be fabricated using this method [196–210]. Figure 10 shows a typical example of nanowires/nanofibers fabrication by electro-spun growth [201]. As shown in Figure 10(a), an appropriate ratio of dimethylformamide, poly(vinyl acetate) (PVA), titanium(IV) propoxide, and acetic acid are mixed as the precursor solution. Then, the solution is loaded into a syringe, which is connected to a high-voltage supply. Afterward, the precursor solution was directly spun onto the Al$_2$O$_3$ substrate with pre-patterned Pt electrode arrays. Finally, nanofibers are pressed under 120 °C to prevent sticking and further calcined in air at 450 °C, and thus TiO$_2$ nanofibers sensors with the mat-like structure are obtained. Due to the simple and inexpensive fabrication process, electrospinning has attracted increasing attention in the commercial field.

![Figure 10](image)

**Figure 10.** (a) Schematic diagram of the processing steps used to fabricate TiO$_2$ nanofiber mats on Al$_2$O$_3$ substrates with interdigitated Pt electrode arrays. PVA (Polyvinyl acetate); and (b) the micrograph of a calcined TiO2 nanofiber mat on top of the Al$_2$O$_3$ substrate (dark region) and Pt electrode (bright region). Reprinted from reference [201] with permission from the American Chemical Society.

3. Metal–oxide Nanowire Devices Fabrication

To study the intrinsic properties of nanowires and use their functionality as a sensing element, one necessary process is transferring nanowires from the growth substrate and integrating them with contact electrodes on a platform. As shown in Figure 11, the current nanowire-based device can be divided into two types: (a) individual nanowire device; and (b) multiple nanowire devices.

![Figure 11](image)

**Figure 11.** Schematic image of (a) an individual nanowire device with different structures (flat, suspended, and vertical); and (b) multiple nanowire device (flat, bridging, and vertical).
3.1. Individual Metal–Oxide Nanowire Device

Due to the fast development of modern electronics, individual metal–oxide nanowire devices such as the field-effect transistor (FET) offer a great chance to explore the electrical, chemical, and mechanical properties of the nanowire.

3.1.1. Device with Flat Structure

A “pick and place” is a common technique in fabricating individual nanowire devices. First, one must “pick” metal–oxide nanowires from the growth substrate. The substrate with nanowires should be immersed in a readily volatile solvent such as isopropanol, ethanol, methanol, and even water. Then, the metal–oxide nanowires are transferred from the growth substrate and dispersed into solvents under the ultrasonic wave. One must then ‘place’ the nanowires. One drop of solvents containing dispersed nanowires should be placed on the platform with pre-deposited electrode pads and dried by simple evaporation. With the assistance of optical scope or SEM observation, the relative positions of nanowires to the pre-deposited markers are recorded. Then, the platform should be covered with a layer of photoresist by spin coating technique. By combining laser/electron-beam lithography and sputtering deposition (or using focused ion beam technique), nanowires can be connected with the electrode pads. Finally, the additional metal and photoresist can be removed by a lift-off process in the organic solvent such as N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and ethanol. The schematic image of the individual nanowire device fabrication process can be seen in Figure 12. Other novel fabrication processes can be seen in the latest review [211].

![Figure 12](image_url)

Figure 12. A schematic diagram illustrating the fabrication processes of individual nanowire devices: (a) substrate; (b) transferring nanowires onto the substrate; (c) photoresist coating (sacrificial layer); (d) sacrificial layer patterning; (e) contact electrode deposition; (f) individual nanowire device after lift-off process.

3.1.2. Device with Suspended Structure

Due to the sensor heating, the hot air near the sensor surface will form a layer which is likely to support convective processes leading to the concentration gradients of reactive analyte gases, termed as stagnant layer [212]. Such a layer can measure up to several tens of nanometers, and it is comparable with the nanowire size, which will cause insufficient exposure to the target molecules [213,214]. To prevent this problem, a suspended structure has been developed to improve sensor performance. The suspended structure is a highly favorable configuration because the nanowires are surrounded by the gas atmosphere. As shown in Figure 13, the fabrication process of a suspended nanowire device is similar to that of a flat nanowire device. However, it requires one more sacrificial layer (inorganic MgO/organic PMMA) before the drop of nanowire solvent (Figure 13b). The overall
enhancement in the performance of the nanodevice is benefited from the suspended structure. For example, Nima et al. fabricated a stable, reproducible ZnO nanowire humidity sensor with a suspended structure [215]. It is observed that the suspended nanowire device presented an exponential change (over five orders) of resistance in response to relative humidity from 0% (dry air) to 60% at room temperature. This improvement is strongly associated with a subthreshold carrier modulation in the nanowire core, the high surface-to-volume ratio of the nanowire, and most importantly, complete exposure of the nanowire surface to air. Owing to the gigantic enhancement in gas sensing response, the development of metal–oxide nanowire gas sensors with the suspended structure has been extensively studied [214,216–220].

Figure 13. A schematic diagram of the individual suspended nanowire device fabrication process: (a) substrate; (b) photoresist coating (sacrificial layer); (c) transferring nanowires onto the substrate; (d) photoresist coating (sacrificial layer); (e) sacrificial layer patterning; (f) contact electrode deposition; and (g) individual nanowire device with suspended structure after the lift-off process.

3.1.3. Device with Vertical Structure

Similar to the suspended nanowire device, sensors with a vertical structure have also been considered a promising design for gas detection due to their 3D architecture. Unfortunately, the conventional “pick and place” technique cannot obtain individual nanowire devices with vertical structures due to the current limitation in nanotechnology. To date, a few papers reported the individual nanowire sensor devices with a vertical structure [221,222]. Offermans et al. offered a potential way to achieve the individual nanowire gas sensor with vertical structure [223,224]. As shown in Figure 14, vertical indium arsenide (InAs) nanowires are firstly grown on an InP(111)B wafer. Then, the nanowires were patterned into arrays ranging in size from 30 µm × 30 µm to 100 µm × 100 µm via combining the sacrificial resist layer and etching process. Finally, using the sacrificial resist layer with sputtering deposition, air bridges were formed to make electrical connections. In view of their device structure, it is possible to achieve a device with fewer nanowire connections or even a single nanowire connection by shrinking the size of the patterned array. Meanwhile, it was shown that this vertical structure of the sensor device presents a very high sensitivity to 100 ppb of NO2 at room temperature. However, due to the uncertainty and complexity of this process, it is impossible to massively fabricate such a device with individual vertical nanowires. To the best of our knowledge, to date, there has been no report using individual metal–oxide nanowires with vertical structure as the gas sensor.
3.2. Metal–Oxide Multiple Nanowire Device

Due to the requirement of precise alignment between the single nanowire and pre-deposited patterned electrodes, the overall fabrication process of the individual nanowire device is complicated, time-consuming, and expensive [225–229]. Furthermore, high accuracy and stable electrical measurement systems are needed to obtain the electrical sensing signals of the single nanowire sensor devices [75]. To simplify the fabrication process and electrical signal measurement, multiple nanowire devices become the most widely accepted device design in practical sensor device applications.

3.2.1. Device with Flat Structure

A mat-like nanowire structure is similar to the single nanowire device with a flat structure, while the fabrication process is much easier than that of the single nanowire device. In a typical mat-like structure, the device can be loaded easily via two steps. As shown in Figure 15, nanowires can be firstly transferred from the growth substrate onto a platform, and then the contact electrodes are deposited by utilizing a mask with sputtering. Alternatively, the electrodes can be firstly pre-deposited on the platform, and finally nanowires are transferred on the surface of electrodes. Both of the two methods are simple, costless, and unnecessary pre/post-process. Due to its convenience in terms of fabrication process, various metal–oxide nanowire gas sensors, including SnO$_2$, ZnO, WO$_3$, TiO$_2$, NiO, CuO [230–235], are successfully obtained by this method. Moreover, this technique is in favor of flexible sensor electronics integration.

3.2.2. Device with Bridging Structure

Due to the easy fabrication, in situ controllable nanowire growth position, and 3D architecture, bridging structure is another promising design for nanowire gas sensors [43,177,191–193,236–267]. In the typical fabrication process of the device with a bridging structure, bottom electrodes should be firstly deposited on the substrate, then a seed/catalyst layer will be deposited on the top of the bottom electrodes. Finally, nanowire will be grown in situ only on the seed/catalyst layer, as shown in Figure 16. With the increase in the growth time, nanowires will incline and contact other nanowires, forming nanowire–nanowire junctions, which can be utilized as a sensing channel for gas detection. Such on-chip growth nanowire sensors can prevent nanowire–electrode contact issues encountered by the flat nanowire sensor devices, and these kind of sensors show a more stable physical and electrical performance than the sensors fabricated by spinning, droppping, or spray coating technique. Park et al. firstly reported a comparison study of NO$_2$ sensing between air-bridged nanowire sensors and conventional nanoparticle sensors [251].
Owing to a higher exposed area to the surroundings, the bridging structure shows a faster response and recovery rates as compared with that of nanoparticle sensors. Meanwhile, Kim et al., Jung et al., and Hung et al. systematically studied the effect of nanowire junction density on the device sensing performance [245, 253, 260]. Through the controlling of nanowire growth time, the number of nanowire–nanowire junctions within the bridging sensor structures can be quantitatively manipulated. Furthermore, it was found that the bridged structures with a high density of junctions show a high sensing performance to NO₂. However, the response and recovery time of the bridging nanowire device with a high density of junctions are slower than that of the low-density nanowire device, because a long time is needed for the molecules’ diffusion in the high density of nanowire network.

![Figure 15. Two typical methods for making a mat-like metal–oxide nanowires device: (a) platform; (b) nanowires transferred onto the platform; (c) contact electrode deposition; (d) contact electrode deposition; and (e) nanowires transferred onto the platform.](image15)

### 3.2.3. Device with Vertical Structure

Recently, the nanowire array sensors with the vertical structure are promising due to their porosity structure and reliable electrical performance [268–270]. To obtain a vertical nanowire sensor, three steps are typically needed, as shown in Figure 17. First, nanowires are grown vertically on the substrate through solution–phase/vapor–phase methods. Then, the nanowires are covered by spin coating a layer of organic photoresist. By precisely controlling the thickness of photoresist on a nanowire array via etching process, the tips of nanowires will be exposed. Afterwards, a metal contact layer is deposited onto the photoresist and connected with all the tips of the nanowires. Finally, a vertical structure of the sensor device can be achieved by removing the unnecessary photoresist. Cao et al. has demonstrated the integration of a vertical WO₃ nanowire sensor with high sensitivity.
to NO₂ [268]. It is shown that the vertical device exhibited the capability to detect NO₂ concentrations down to the 50 ppb level, which shows a promising future in the field of low concentration gas detection. In addition, Chen et al. has proposed a sensor array composed of vertical device structures with different noble metal decorations (Pd, Pt, and Au) for selective gases detection [48]. Several different types of sensors are fabricated via altering the selection of decorating materials.

![Figure 17](image-url)

**Figure 17.** A typical method for making a vertical metal–oxide nanowires device: (a) the substrate with the seed/catalyst layer; (b) nanowires are grown vertically; (c) photoresist coating with the further etching process; and (d) top contact electrode deposition and the removal of photoresist.

### 4. Current Progress in Performance Tailoring of Metal–Oxide Nanowire-Based Gas Sensors

Although metal–oxide nanowires have already shown great potential as gas sensing materials, further efforts are still encouraged to enhance the sensing performance of nanowire-based sensor electronics, such as gas species discrimination from mixtures, low concentration, and room temperature detection. To achieve such goals, introducing additives on the nanowire surface has been proved to be an easy and effective approach.

#### 4.1. Nanoparticles Decoration (NPs Decoration)

The loading of noble metal/oxide nanoparticles with a nanometer size onto a metal–oxide nanowire surface has been widely employed for functionalizing the nanowire-based sensors due to their low cost and simplicity in the fabrication process. Here, we introduce one common method (not least) to load nanoparticles on nanowires. For noble metal nanoparticle decoration as an example, a noble metal (M) precursor solution was firstly prepared by dissolving appropriated HMClₓ·H₂O into H₂O (ethanol, etc.). Then, by simply immersing nanowires in the above solution for a proper time and calcined at high temperature, M-loaded nanowires can be obtained. This method can also be used for metal–oxide nanoparticle decoration, despite using different precursors. Currently, there are two coexisting mechanisms to understand the sensing performance of decorated nanowires: (1) chemical sensitization (spillover effect): noble metal nanoparticles can promote the dissociation of molecules and oxygen on nanowire surface, leading to an efficient chemical reaction. Moreover, owing to the noble metal-induced lower energy barrier for gas adsorption and desorption, the response and recovery rates can be accelerated [271]; (2) electronic sensitization: the interface between oxidized noble metals (or oxide nanoparticles) and nanowires usually form a thicker electron depletion layer with a narrow channel. During exposure to the target molecules, the concentration of charge carriers can be efficiently modulated [272]. To date, researchers have made significant progress in fabricating nanoparticles decorated nanowire sensors. Through optimizing the decorated material selection/combination, the size of nanoparticles, and the surface coverage of nanowires, it is accessible to realize the fabrication of functionalized nanowire sensors with high sensitivity, high selectivity, and low working temperature. A detailed overview of the sensing performance of noble metal-decorated metal–oxide nanowire gas sensors is summarized in Table 1.
As for sensitivity, Kolmakov et al. firstly reported the use of noble metal (Pd) functionalized with metal–oxide nanowire (SnO₂) device for the sensitivity enhancement [273]. As shown in Figure 18 d, due to (1) oxygen dissociation on Pd nanoparticles by spillover effect, and (2) the diffusion of weakly adsorbed oxygen on nanowire surface to Pd nanoparticles, it is found that the Pd nanoparticles decoration can dramatically enhance the device sensing performance to O₂ and H₂. Motivated by this encouraging result, to date, tremendous efforts via noble metal/oxide nanoparticles decoration are being intensively investigated for enhancing device sensitivity [87,273–277].

![Figure 18. (a–c) Nanoparticles decorated metal–oxide nanowire with different coverage; (d) schematic depiction of the three major processes taking place at a SnO₂ nanowire surface and their band diagram; and (e) compared studies of the sensing performance of SnO₂ and SnO₂/Pd nanowire sensor devices. Reprinted from reference [273] with permission from the American Chemical Society.](image-url)

Nanoparticle decoration is also an alternative way to dramatically improve the selectivity of the nanowire-based sensors [174,272,274–286]. For example, Kim et al. reported a ZnO nanowire sensor with high sensitivity and selectivity toward H₂ via Pd nanoparticle decoration [274]. Due to the synergistic effect of chemical sensitization of Pd nanoparticles and metallization effect of ZnO, the sensing response to H₂, O₂, NO₂, C₆H₆, and C₇H₈ are increased by 3214.1, 1.6, 7.8, 17.2, and 166.9%, respectively. Moreover, compared with pristine nanowire, the Pd-decorated ZnO nanowire shows a capability to detect 0.1 ppm H₂ with a wide temperature range from 150 to 350 °C. Byoun et al. reported a TeO₂ nanowires gas sensor by surface decoration with oxide nanoparticles [280]. Due to the formation of p–n heterojunctions between p-type TeO₂ nanowire and n-type ZnO nanoparticles, the TeO₂ nanowires become more resistant and suitable for sensing oxidizing gas, especially since it shows an excellent NO₂ selectivity in comparison with interfering gases such as SO₂, CO, and C₂H₅OH.

Furthermore, surface decoration with noble metal/oxide nanoparticles has been regarded as an effective way in lowering down the sensor operation temperature [280,287–295]. For example, as reported by Liang et al., due to the spillover effect and the change in depletion layer caused by Au nanoparticles, the Au decorated VO₂ nanowires sensor exhibits an excellent sensing performance to NO₂ at 0.5–5 ppm at room temperature [285]. Lupan et al. have reported that Au nanoparticle decoration on ZnO nanowire surface can realize the H₂ room temperature detection [289], Choi et al. found that Pd nanoparticles decoration on
ZnO nanowires enables the CO sensing at room temperature [287] and Hong et al. have reported the Cu$_2$O nanoparticles-decorated ZnO nanowire sensor could realize the room temperature sensing of NO [296].

In addition, the effects of decorated nanoparticle size and density have also been intensively investigated [192,271,282,296,297]. For example, Lee et al. have studied the size effect of Au nanoparticles on the CuO nanowire sensor [192]. As the diameter of Au nanoparticles decreases, the sensing responses of the nanowire sensor present an increase to NO$_2$ and CO, and a maximum performance appears when 60 nm of Au nanoparticles are decorated on the CuO nanowire surface. Meanwhile, they have pointed out that the size of nanoparticles should be carefully optimized to prevent sufficient surface coverage, since excessive surface coverage would cause the steric hindrance on the nanowire surface, which is harmful to gas sensing.

Table 1. A detailed overview of sensing performance of noble metal-decorated metal–oxide nanowire gas sensors.

<table>
<thead>
<tr>
<th>NWs</th>
<th>NPs</th>
<th>Target Gas</th>
<th>$T_{oper}$ (°C)</th>
<th>LOD (ppm)</th>
<th>Response</th>
<th>Response Time(s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>Ag</td>
<td>NH$_3$</td>
<td>450</td>
<td>0.05</td>
<td>300 @ 100 ppm</td>
<td>45</td>
<td>[298]</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>NO$_2$</td>
<td>200</td>
<td>0.1</td>
<td>2 @ 0.1 ppm</td>
<td>N/A</td>
<td>[299]</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>NO$_2$</td>
<td>300</td>
<td>2</td>
<td>13 @ 10 ppm</td>
<td>118</td>
<td>[300]</td>
</tr>
<tr>
<td></td>
<td>Au/ZnO-branching</td>
<td>CO</td>
<td>300</td>
<td>0.0026</td>
<td>26.6 @ 0.1 ppm</td>
<td>75</td>
<td>[301]</td>
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<td></td>
<td>Pd</td>
<td>H$_2$</td>
<td>300</td>
<td>1</td>
<td>55.72 @ 100 ppm</td>
<td>22</td>
<td>[302]</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>NO$_2$</td>
<td>300</td>
<td>0.1</td>
<td>505 @ 0.1 ppm</td>
<td>20</td>
<td>[271]</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>H$_2$</td>
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<td>1</td>
<td>16.95 @ 1 ppm</td>
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<td>[88]</td>
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<td>700 @ 0.1 ppm</td>
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<td>[271]</td>
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<td>N/A</td>
<td>1.87 @ 1000 ppm</td>
<td>0.33</td>
<td>[288]</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>Ethanol</td>
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<td>6.5 @ 100 ppm</td>
<td>N/A</td>
<td>[304]</td>
</tr>
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<td>18 @ 100 ppm</td>
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<td>[304]</td>
</tr>
<tr>
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<td>Acetone</td>
<td>300</td>
<td>0.1</td>
<td>5.8 @ 100 ppm</td>
<td>N/A</td>
<td>[304]</td>
</tr>
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<td>H$_2$</td>
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<td>0.1</td>
<td>4 @ 100 ppm</td>
<td>N/A</td>
<td>[304]</td>
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<td>Toluene</td>
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<td>58 @ 100 ppm</td>
<td>N/A</td>
<td>[304]</td>
</tr>
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<td></td>
<td>Pd</td>
<td>Ethanol</td>
<td>260</td>
<td>-</td>
<td>5 @ 500 ppm</td>
<td>6</td>
<td>[305]</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>Ethanol</td>
<td>450</td>
<td>5</td>
<td>228.1 @ 100 ppm</td>
<td>40–80</td>
<td>[306]</td>
</tr>
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<td>Au</td>
<td>NO$_2$</td>
<td>150</td>
<td>1</td>
<td>31.4 @ 1 ppm</td>
<td>29</td>
<td>[284]</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>NO$_2$</td>
<td>25(UV)</td>
<td>1</td>
<td>2.6 @ 1 ppm</td>
<td>39.5</td>
<td>[292]</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>H$_2$</td>
<td>25</td>
<td>&lt;1 ppm</td>
<td>40 @ 100 ppm</td>
<td>N/A</td>
<td>[289]</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>Acetone</td>
<td>172</td>
<td>15</td>
<td>50.5 @ 100 ppm</td>
<td>1</td>
<td>[307]</td>
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<td>Au</td>
<td>H$_2$</td>
<td>25</td>
<td>20</td>
<td>32.9 @ 1000 ppm</td>
<td>N/A</td>
<td>[302]</td>
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<td>ZnO</td>
<td>Au/Fe$_2$O$_3$</td>
<td>NO$_2$</td>
<td>400</td>
<td>150</td>
<td>247 @ 250 ppm</td>
<td>N/A</td>
<td>[308]</td>
</tr>
<tr>
<td></td>
<td>Au/Pd</td>
<td>NO$_2$</td>
<td>100</td>
<td>1</td>
<td>94.2 @ 1 ppm</td>
<td>35</td>
<td>[309]</td>
</tr>
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<td></td>
<td>Pd</td>
<td>Benzene</td>
<td>25(UV)</td>
<td>0.0067</td>
<td>2.2 @ 50 ppm</td>
<td>N/A</td>
<td>[310]</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>H$_2$</td>
<td>350</td>
<td>1</td>
<td>87 @ 100 ppm</td>
<td>N/A</td>
<td>[274]</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>H$_2$S</td>
<td>300</td>
<td>10</td>
<td>20 @ 500 ppm</td>
<td>720</td>
<td>[311]</td>
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<td></td>
<td>Pd/BN</td>
<td>H$_2$</td>
<td>200</td>
<td>0.1</td>
<td>12.3 @ 50 ppm</td>
<td>240</td>
<td>[307]</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>H$_2$S</td>
<td>260</td>
<td>0.0011</td>
<td>65 @ 0.3 ppm</td>
<td>40</td>
<td>[312]</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>Toluene</td>
<td>25(UV)</td>
<td>0.0003</td>
<td>2.86 @ 50 ppm</td>
<td>N/A</td>
<td>[310]</td>
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<tr>
<td>WO$_3$</td>
<td>Au</td>
<td>n-butanol</td>
<td>250</td>
<td>5</td>
<td>147 @ 100 ppm</td>
<td>16.5</td>
<td>[313]</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>Acetone</td>
<td>250</td>
<td>5</td>
<td>72 @ 200 ppm</td>
<td>17.5</td>
<td>[313]</td>
</tr>
<tr>
<td></td>
<td>Pd/Au</td>
<td>Acetone</td>
<td>300</td>
<td>200</td>
<td>152.4 @ 200 ppm</td>
<td>96</td>
<td>[314]</td>
</tr>
<tr>
<td></td>
<td>Pd/Au</td>
<td>n-butanol</td>
<td>200</td>
<td>5</td>
<td>93 @ 50 ppm</td>
<td>12</td>
<td>[315]</td>
</tr>
<tr>
<td></td>
<td>Rh</td>
<td>Acetone</td>
<td>300</td>
<td>0.2</td>
<td>78 @ 5 ppm</td>
<td>11</td>
<td>[316]</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>Acetone</td>
<td>350</td>
<td>0.05</td>
<td>78 @ 5 ppm</td>
<td>11.7</td>
<td>[202]</td>
</tr>
<tr>
<td>W$<em>{18}$O$</em>{49}$</td>
<td>Ag/Pt</td>
<td>Trimethylamine</td>
<td>240</td>
<td>0.071</td>
<td>22 @ 2 ppm</td>
<td>15</td>
<td>[277]</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>Ag</td>
<td>Ethanol</td>
<td>25</td>
<td>0.5</td>
<td>1900 @ 100 ppm</td>
<td>N/A</td>
<td>[317]</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>CO</td>
<td>25</td>
<td>0.5</td>
<td>2200 @ 100 ppm</td>
<td>N/A</td>
<td>[317]</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>H$_2$</td>
<td>25</td>
<td>0.5</td>
<td>1400 @ 100 ppm</td>
<td>N/A</td>
<td>[317]</td>
</tr>
</tbody>
</table>
4.2. Branched Nanowire

In addition to surface decoration, branched nanowires (nanowire hierarchical nanostructures) offer a high specific surface area for gas diffusion and adsorption, which are beneficial for molecular sensing. Khoang et al. reported a controllable and scalable route for preparing n-type ZnO branched n-type SnO$_2$ nanowire hierarchical nanostructures via a combination of thermal evaporation method (SnO$_2$ nanowires) and hydrothermal method (ZnO nanowires). As shown in Figure 19, compared with pure SnO$_2$ nanowires, the branched nanowires sensor shows three-five-fold sensitivity enhancement to 25–500 ppm ethanol. Kaur et al. demonstrated an n-type ZnO branched p-type NiO nanowire hierarchical structures for sensing performance enhancement [233]. In such a kind of sensor, the surface of NiO nanowires is fully covered by ZnO nanowires, leading to a response mode transformation from the p-type to n-type. In addition, the lowest detection limits of these sensors to ethanol and acetone can be down to 7 and 11 ppm, respectively.

Moreover, to further improve the device sensing performance, Choi et al. attempted to decorate Au nanoparticles on the ZnO branched SnO$_2$ nanowire surface [300]. It was indicated that the sensing response of the ZnO-branched SnO$_2$ nanowire sensor is dramatically enhanced after Au nanoparticle decoration due to the spillover effect of noble metal. Meanwhile, the sensor shows an excellent selectivity toward NO$_2$. Similar results have also been reported recently by Bang et al. [320]. They realized the low temperature and selective NO$_2$ sensing via using synergistic effects of Pt decoration and Bi$_2$O$_3$ branching.

<table>
<thead>
<tr>
<th>NWs</th>
<th>NPs</th>
<th>Target Gas</th>
<th>$T_{\text{oper}}$ (°C)</th>
<th>LOD (ppm)</th>
<th>Response</th>
<th>Response Time(s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>Au</td>
<td>NO$_2$</td>
<td>300</td>
<td>1</td>
<td>2.2 @ 50 ppm</td>
<td>N/A</td>
<td>[192]</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>CO</td>
<td>350</td>
<td>1</td>
<td>1.25 @ 50 ppm</td>
<td>N/A</td>
<td>[192]</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>Ethanol</td>
<td>200</td>
<td>1000</td>
<td>3.8 @ 1000 ppm</td>
<td>480</td>
<td>[318]</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>H$_2$</td>
<td>200</td>
<td>1000</td>
<td>4.5 @ 1000 ppm</td>
<td>600</td>
<td>[318]</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>H$_2$S</td>
<td>100</td>
<td></td>
<td>1.9 @ 100 ppm</td>
<td>N/A</td>
<td>[319]</td>
</tr>
<tr>
<td>PdO</td>
<td>Pt</td>
<td>H$_2$</td>
<td>25</td>
<td>10</td>
<td>1.2 @ 100 ppm</td>
<td>166</td>
<td>[290]</td>
</tr>
<tr>
<td>VO$_2$</td>
<td>Au</td>
<td>NO$_2$</td>
<td>25</td>
<td>0.5</td>
<td>3.22 @ 5 ppm</td>
<td>N/A</td>
<td>[285]</td>
</tr>
</tbody>
</table>

NWs: nanowires; NPs: nanoparticles; $T_{\text{oper}}$: operation temperature of sensor; LOD: limit of detection; Response: R$_g$/R$_a$ (Oxidizing gas) or R$_a$/R$_g$ (Reducing gas).

Figure 19. Left figure: branches nanowire with different length on ZnO nanowires: (a) as fabricated ZnO nanowires; (b) 1 h growth SnO$_2$ branched ZnO nanowire; (c) 2 h growth; (d) 4 h growth. Right figure: SnO$_2$ nanowire and SnO$_2$–ZnO hierarchical structure sensing performance; (e) as fabricated ZnO nanowires; (f) 1 h growth SnO$_2$ branched ZnO nanowire; (g) 2 h growth; and (h) 4 h growth. Reprinted from reference [321] with permission from the American Chemical Society.
4.3. Core–Shell Structure (C–S Structure)

Core–shell (C–S) metal–oxide nanowire sensors have also been extensively studied due to their ability to detect an extremely low concentration of chemical species and mitigate the poor selectivity [322,323]. The C–S structure is similar to the nanoparticle-decorated structure but with a continuous layer and higher stability [271]. Such a shell layer can serve as a catalytic layer to promote the molecular oxidizing [324], narrow the conduction core part of nanowire [325], facilitate the adsorption of gas molecules to increase the sensing activity [326], and work as a main conductive channel for sensing [327]. Currently, various C–S nanowires with a combination like n–n (n-type core/n-type shell) [323,327–330], n-p (n-type core/p-type shell) [256,331], and p-n (p-type core/n-type shell) [252,324,332] have been employed as gas sensors. According to recent C–S nanowire gas sensors, the shell layer selection and its deposition thickness are crucially important to tailor the performance of the nanowire-based gas sensors [332,333].

Park et al. firstly demonstrated an exciting model to understand the sensitivity enhancement in SnO2-ZnO C–S nanofibers [328]. As the deposition shell thickness is comparably shorter than or equivalent to the Debye length of the shell materials, the conducting channel can be fully depleted during the exposure to target molecules. As a result, the conductance variation is favorably considerable compared with that of the non-C–S structure. Katchoch et al. also reported a similar result via systematically studying the impact of shell thickness on the sensing performance of core/shell structures [330]. By gradually changing the thickness of ZnO on SnO2 nanofibers, it was observed that the nanofiber sensor device has the highest sensing response towards CO when 20 nm of ZnO shell is loaded on the SnO2 nanofiber surface. Such thickness is identically close to the Debye length of ZnO.

As shown in Figure 20a–c, by controlling the ALD growth time of the shell layer, Choi et al. proposed a dual functional sensing mechanism in the SnO2/ZnO C–S nanowires [327]. First, as the shell layer is thinner than its Debye length, the shell layer will experience a large resistance modulation during the sensor exposure to reducing gas. As a result, a substantial portion of electron transport occurs through the inner core nanowire, which would weaken its sensing performance. Second, as the shell layer is slightly larger than its Debye length, electrical transport will be mostly confined within the shell layer, leading to a high modulation/response in sensing performance.

Figure 20. (a) Nanowire with SnO2 core and ZnO shell structure; (b) EDS of core–shell nanowire; (c) shell thickness-dependent sensing performance towards CO, benzene, toluene, and NO2. Reprinted from reference [327] with permission from the American Chemical Society. (d,e) Schematics of the hydrogen-sensing mechanism for In2O3 nanowires and In2O3/ZnO C–S nanowires sensors. Reprinted from reference [334] Copyright 2011 Elsevier.
Singh et al. have discussed carrier transport based on In$_2$O$_3$ nanowires and In$_2$O$_3$/ZnO core–shell nanowires network devices [334]. Due to the large resistance of the polycrystalline ZnO shell, carriers mainly flow through the single crystalline In$_2$O$_3$ core. To achieve electron transportation from nanowire to nanowire, only one potential barrier (core–core, C/C) has to be overcome in the In$_2$O$_3$ nanowires device (Figure 20d), while the electrons are essentially to overcome three potential barriers (core to shell (C/S), shell to shell (S/S), and shell to core (S/C)) in the core–shell nanowire devices (Figure 20e). Owing to the modulation of potential barriers, significant enhancements in sensor response for the reducing gases have been achieved. This mechanism also can be used to explain the sensing performance enhancement in other p/n and n/p types of core/shell nanowire sensors [256,325,329,331,335].

4.4. Impurities Doping

Introducing dopants have a significant impact on the electrical and chemical properties of semiconductor metal–oxides [336–338]. Experimental studies have proved that small amounts of impurity additives (< 0.1 at% or lower) can significantly alter the electronic and chemical properties of metal–oxide nanowires due to the modulation of the Fermi level and introducing additional adsorption sites [339]. For example, Zhang et al. have studied the oxygen vacancies doping effect in In$_2$O$_3$ nanowires for NH$_3$ sensing [340]. According to their report, via varying the concentration of oxygen vacancies in In$_2$O$_3$ nanowires, the Fermi level (E$_F$) of the In$_2$O$_3$ nanowires can be controlled close to the conduction band and above the energy level of NH$_3$ (E$_{NH_3}$) in a heavily doped condition, or the Fermi level (E$_F$) can be below E$_{NH_3}$ in a relatively low doping concentration. As shown in Figure 18a, when the E$_F$ of nanowires is higher than E$_{NH_3}$, electrons should transfer from the nanowire to the adsorbed NH$_3$ and result in a reduction in the nanowire carrier concentration. When the E$_F$ of nanowires is lower than E$_{NH_3}$, electrons should migrate from adsorbed NH$_3$ to the nanowire and result in an enhanced conductance, as shown in Figure 21a,b. This work indicates that the density of dopants can determine the signal and amplitude of the nanowire sensor response. Moreover, Singh et al. have reported an approach to tune the Fermi level of In$_2$O$_3$ nanowires via Zn doping and achieving the room temperature detection of CO [341]. As shown in Figure 21c,d, due to the small chemical potential gradient between the adsorbed CO molecule and Fermi level of undoped In$_2$O$_3$ nanowires, there is less electron transfer (to reach equilibrium) and the nanowire-based sensor shows a poor sensitivity to CO at room temperature. In contrast, as shown in Figure 21e,f, a big difference of the chemical potential between the Fermi level of nanowire and CO molecule is presented after In$_2$O$_3$ nanowires are doped with Zn, as a result, the Zn doped In$_2$O$_3$ nanowire sensor device offers a fast (response time 20s and recovery time 10s) and large transfer of electrons (1–5 ppm CO detection). However, due to the difficulties in introducing impurities into single-crystalline nanowires, impurities doping is less popular than nanoparticles decoration, branched structures, and core–shell structures for achieving high-performance device.
5. Gas Sensing Mechanism

Today, nanowire chemiresistors are being widely investigated due to their convenience in data analysis, high accuracy, low cost, and their ability to dynamically monitor the channel resistance/conductance variation during the exposure to the target molecules. Generally, the sensing mechanism of chemiresistors can be divided into three types.

5.1. Ohmic-Contacted Sensing

In a traditional chemiresistor sensor, Ohmic contact is highly preferred to study the intrinsic properties of nanowires. Generally, the classical D–L model is responsible for the sensitivity of nanowire gas sensors, where D represents nanowire diameter (D), and L represents the depth of the surface depletion layer (L) [342,343]. Considering the n-type oxide case, when a sensor is exposed to the atmosphere, oxygen can be adsorbed on the surface of metal–oxide nanowire and becomes negatively charged by the following equations [22]:

\[
\text{O}_2(\text{gas}) \leftrightarrow \text{O}_2(\text{ads})
\]  

(1)
O\(_2\)\text{(ads)} + e^- \leftrightarrow O^-(\text{ads}) < 100 \, ^\circ \text{C} \tag{2}

O^-(\text{ads}) + e^- \leftrightarrow 2O^- (\text{ads}) 100-300 \, ^\circ \text{C} \tag{3}

O^-(\text{ads}) + e^- \leftrightarrow O^{2-} \text{(ads)} > 300 \, ^\circ \text{C} \tag{4}

Such oxygen-charged behavior would extract electrons and create a shell-like surface depletion layer on the nanowire surface (Figure 22a), which can effectively modulate channel conductivity. Moreover, due to the adsorbed oxygen ions (O^- and O^{2-}), highly active towards reducing gas, high temperatures (>100 °C) are usually required to generate oxygen ions and enhance chemical reaction. For example, when the sensor is exposed to the gases (such as toluene, ethanol, CO, NH\(_3\), H\(_2\), methanol, shown in Equations (5)-(7) [22]), the charged oxygen (O^-) can react with these gases, and release electrons back to the nanowire bulk. As a result, the thickness of the depletion layer is shrunk, leading to an increase in conductance (Figure 22b). In contrast, when the sensor is exposed to the oxidizing gases (such as NO\(_2\), O\(_3\), Equations (8) and (9) [22]), these gases can extract more electrons from the nanowire surface. Then, the depletion layer thickness increases and results in a reduction in nanowire conductance (Figure 22c):

\begin{align*}
\text{CO(ads)} + O^- (\text{ads}) & \rightarrow \text{CO}_2 (\text{gas}) + e^- \tag{5} \\
\text{CH}_3\text{CH}_2\text{OH} (\text{ads}) + 6O^-(\text{ads}) & \rightarrow 2\text{CO}_2 (\text{gas}) + 3\text{H}_2\text{O} (\text{gas}) + 6e^- \tag{6} \\
\text{H}_2(\text{ads}) + O^- (\text{ads}) & \rightarrow \text{H}_2\text{O} (\text{gas}) + e^- \tag{7} \\
e^- + \text{NO}_2(\text{ads}) & \leftrightarrow \text{NO}_2^-(\text{ads}) \tag{8} \\
2e^- + \text{O}_3(\text{ads}) & \leftrightarrow \text{O}_2^- (\text{ads}) + O^- (\text{ads}) \tag{9}
\end{align*}

Figure 22. A schematic diagram of conventional chemiresistor sensors: (a) nanowire conducting channel exposed to ambient; (b) nanowire conducting channel exposed to reducing gases; and (c) nanowire conducting channel exposed to oxidizing gases.

Due to its convenience in data analysis, tremendous works have used the Ohmic contacted device as a platform for fundamental studies to improve the device sensing performance.

5.2. Schottky-Contacted Sensing

Recently, the Schottky-contacted nanowire sensors have attracted considerable attention due to the higher sensitivity, faster sensing response, shorter recovery time, and lower cost as compared with the conventional Ohmic-contacted nanowire sensors. In a typical Schottky-contacted sensor (Figure 23a), the overall resistance/conductance of the device is dominated by the Schottky barrier height (SBH), and its value is susceptible to external stimulus. Wei et al. firstly reported a Schottky-contacted nanowire sensor for gas molecules detection [344]. The device contains one Pt/ZnO junction (Schottky contact) and one Pt–Ga/ZnO junction (Ohmic contact). By comparing the sensing performance of the Schottky-contacted device and the conventional Ohmic-contacted device, it is shown that the Schottky-contacted sensor device presents 1085 times and 8776 times sensitivity
improvement to oxidizing gas (O\(_2\)) and reducing gas (CO), respectively. Furthermore, the Schottky contacted sensor device exhibited a faster response and shorter reset time, improved by a factor of 7. This new sensing concept has been extensively applied to other metal–oxide nanowire systems such as the well-known SnO\(_2\) [345] and In\(_2\)O\(_3\) [346] nanowire-based sensors. Here, the author recommends the latest comprehensive review of Schottky-contacted nanowire sensors presented by Meng et al. [21].

![Figure 23. A schematic diagram of Schottky-contacted sensors: (a) structure of a Schottky-contacted sensor; and (b) change of Schottky barrier height and depletion region under the external stimulation.](image)

### 5.3. Nanowire–Nanowire Junctions Sensing

In the case of an n-type nanowire–nanowire junction sensor, as shown in Figure 24a, both the thickness of the electron depletion layer and the potential barrier height of the nanowire–nanowire interface dominates the overall conductance of the device. Furthermore, if the electron depletion layer is smaller than the nanowire diameter, the potential barrier heights of nanowire–nanowire junctions will play a crucial role in the gas sensing performance of nanowire sensors. Similar to the Schottky-contacted nanowire devices, the nanowire–nanowire barrier height can be decreased/increased when devices are exposed to a reducing/oxidizing atmosphere.

![Figure 24. A schematic diagram of conventional nanowire–nanowire junction sensors: (a) nanowire conducting channel exposed to ambient; (b) nanowire conducting channel exposed to oxidization gas; and (c) nanowire conducting channel exposed to reducing gas.](image)

Many works have been performed using the interfacial sensing concept, not only for the simplicity in device fabrication but also for higher sensitivity. Most importantly, this concept also shows strong integration capability onto a sensing platform due to the development of nanowire devices with bridging structures [246]. Park et al. firstly reported a metal–oxide nanowire sensor with a bridging structure for NO\(_2\) detection [251]. As reported in their work, SnO\(_2\) nanowires are in situ grown at the pre-deposited electrode on-chip without using any arduous and individual lithography process. Due to self-connection with other nanowires, multiple nanowire–nanowire junctions are naturally formed as sensing channels. Consistent gas sensing characteristics can be seen due to the averaging effect of multi nanowire connections, and high sensitivity to NO\(_2\) is obtained (R\(_g\)/R\(_a\) = 230). Inspired by their encouraging work, other metal–oxide nanowires (ZnO, TiO\(_2\), and CuO)
have also been applied to fabricate bridging structure sensors to combine the merits of in situ growth and nanowire–nanowire junctions sensing [177,191,250,263,347].

6. Critical Issues for Metal–Oxide Nanowire-Based Gas Sensor Devices

Despite all the extraordinary achievements of 1D nanowire-based sensors, some critical problems are still encouraged to be studied and investigated further to advance the nanowire sensor from the lab to the market. Here, we mainly discuss four critical issues: reproducibility, selectivity, stability, and energy consumption.

6.1. Reproducibility of Devices

Integrating a nanowire with contact electrodes on a platform allows us to study the intrinsic properties of the nanowire. However, a tiny variation in the size or shape of nanostructures will powerfully alter their physical and chemical properties. Thus, the nanowire-based electronics would inevitably suffer from poor reproducibility. To prevent the reproducibility issue, one easy method is to use a multiple nanowire sensor to eliminate the individual differences among nanowires. Currently, a commercially available fabrication process for the thin film sensor is used for the mat-like nanowire network sensor fabrication. Zhang et al. have compared the difference in electrical properties between single and multiple nanowire sensors [75]. It was found that all the multiple nanowire devices possess similar and consistent characteristics such as conductance, threshold gate voltage, and sensitivity to gas species. The fabrication of multiple nanowire gas sensors with the bridging structure is also an alternative approach to obtain molecular sensors with high uniformity [247]. The fabrication process in detail was described in Section 3.2.2. Unfortunately, those sensors did not really face/solve the reproducibility issues in the single nanowire devices. In fact, there is no difference between using multiple nanowire devices and conventional nanoparticle devices for gas sensing despite the porous structure.

6.2. Selectivity of Device

Another critical issue is the selectivity of the sensor device. Metal–oxide nanowire sensors generally have high sensitivity to the gas analytes, but they are also suffering from poor selectivity. To enhance the selectivity of sensors, a widely accepted method is introducing recognition elements on the sensing materials, for example, impurity elements doping, nanoparticle surface decorating, core/shell heterostructure construction. In addition, operational temperature modulation and nanowire architecture altering are also served as effective methods to improve the selectivity of the metal–oxide nanowire-based molecular sensors toward the target gas molecules. However, the results are usually far from prospects due to the low operational stability.

In addition, an alternative way to selectively detect the target gas molecules is to use the sensor array, because sensor arrays combined by a number of non-selective sensors which can acquire more information on a specific analyte than an individual sensor [348]. Subsequently, molecule information can be extracted from sensor arrays by appropriate pattern recognition techniques, such as principal component analysis (PCA) and back-propagation artificial neural network (BP-ANN) [349]. However, according to the research from Chen et al., multi-component sensing combined with PCA cannot work well if the reactions have no big difference between a specific target species and different metal–oxide surfaces [350]. Thus, enhancing the overall sensing performance of functional materials is the priority rather than data extraction and process. Unfortunately, this is usually not an easy task.

6.3. Long-Term Stability of the Device

Stability, including chemical stability and physical stability, is the essential key to open the gate for sensor practical applications. Sysoev et al. firstly pointed out that using the nanowire network sensor can obtain long-term stable sensing performance compared with the conventional nanoparticle sensors because nanowires can prevent nanostructure
aggregation [351]. However, although numerous efforts are devoted to improving the long-term stability of metal–oxide nanowire sensors, the influence of humidity, poisoning, and new contact issues still exist to prevent such a kind of sensors from the practical applications [47]. Steinhauer et al. reported that the sensing performance of CuO nanowire-based gas sensors is strongly weakened with the increase in surrounding H$_2$O [47]. This is because the formation of the surface hydroxyl groups induced by H$_2$O adsorption prevents the oxygen chemisorption from the surface active sites. Meanwhile, Nakamura et al. have noticed that a ppm-level CO$_2$ in the air can react substantially with ZnO nanowire surfaces even at room temperature [74]. Such a reaction will form an electrically insulating zinc carbonate thin layer, which can critically determine the electrical stability of hydrothermally grown single-crystalline ZnO nanowires. In addition, Zeng et al. reported a contact issue in the conventional metal–oxide nanowire device [73]. Titanium has been most widely used to contact typical metal–oxide (e.g., SnO$_2$, ZnO) by counting the energy level matching and good adhesion to the substrate, while the Ti contact can be oxidized easily, which causes an increase in contact resistance and further degradation in sensor performance after long-time operations under high temperature. Up to now, only a few papers have mentioned how to achieve long-term stability for metal–oxide nanowire sensors, and it is still remains a crucial challenge for commercialization.

6.4. Energy Consumption

An external heater is usually needed to elevate the temperature of metal–oxide gas sensors for effective gas sensing, which inevitably increases the power consumption and sensor size. There are currently two methods to solve this problem: (1) developing room temperature sensing materials; (2) using the self-Joule-heat technique. As for low-temperature sensors, tremendous progress has been made to reduce the operating temperature of the metal–oxide nanowire sensors, such as surface modification, additives doping, UV/visible-light irradiation. For example, Lupan et al. reported that the Pd-modified ZnO nanowires sensor could achieve room temperature sensing for H$_2$. However, it appears to have other annoying troubles such as lower sensing response, longer response time, and slow recovery rate [352]. Self-Joule-heating is a nearly ideal strategy for operating nanowire gas sensors at ultralow power consumption, without additional heaters. Currently, it has been reported that conducting self-Joule-heat for nanowire sensors and remarkably decrease power consumption. Prades et al. have reported that the energy consumption of individual SnO$_2$ nanowire sensor devices can be down to 20 µJ/s as self-Joule-heat is performed [218]. In addition, the power consumption of the nanowire sensor device could be further decreased via the pulsed self-heating technique [353]. However, recent studies on the self-Joule-heat technique only focused on controlling the spatial thermal properties of nanowires rather than tailoring the sensing performance of these sensors.

7. Prospective towards Metal–Oxide Nanowire Gas Sensor Electronics

As for the reproducibility of nanowire devices, we should carefully consider how to synthesize nanowires with high uniformity. Template-assisted nanowire growth is considered an alternative approach to achieve a highly ordered nanowire array. However, the complexity of template fabrication, low density of nanowires, and the extensive distribution of nanowire diameter have limited the wide application of such method [354]. Recently, Zhao et al. reported a two-step method to fabricate ZnO nanowires with uniformly shaped structures, as shown in Figure 25 [355]. Firstly, ZnO nanowires of random size are etched by NH$_4^+$ as the seed layer, and then, a very similar diameter (average about 17 nm with σ 1.3 nm, shown in Figure 25c) of ZnO nanowires are grown in the second step, which significantly increases the reproducibility of metal–oxide nanowire. This unique finding paves the way for the fabrication of nanowires-integrated nanodevices with reliable performance.
Poor selectivity is a perpetually perplexing problem that limits the wide application of the MOS gas sensor, including the metal–oxide nanowire-based sensors. Inspired by the catalytical chemistry, it is worth considering combining porous materials such as zeolites, metal–organic frameworks, and mesostructured oxides with a metal–oxide nanowire [356–358]. Canlas et al. reported a novel method to fabricate molecules imprinted oxide catalyst, and the fabrication process is shown in Figure 26 [359]. Using this structure, the nanocavities can preferentially react with nitrobenzene rather than nitroxylene in the photoreduction model and react with benzyl alcohol rather than 2,4,6-trimethylbenzyl alcohol in the photo-oxidation model. This technique can be applied to the metal–oxide nanowire sensor to gigantically improve selectivity due to their preferential interactions with specific VOC molecules, even with a chemically similar structure.

Figure 25. (a) SEM image of two-step growth ZnO nanowire; (b) SEM image of conventional single-step growth ZnO nanowire; (c) comparison of ZnO nanowire diameter distribution grown by single-step and two-step method; (d) the mechanism of the synthesis of monodispersed sized ZnO nanowires from randomly sized seeds. Reprinted from reference [355] with permission from the American Chemical Society.

Figure 26. (a) The fabrication process of molecules imprinted oxide; and (b) the preferential reaction with gas species. Reprinted from reference [359] with permission from the Nature publishing group.
Solving the degradation issues, including nanowire degradation, contact degradation, and electrode degradation, is the only way to achieve long-term stability in nanowire devices. As shown in Figure 27a, Nakamura et al. demonstrated a strategy for achieving the atmospheric electrical stability of ZnO nanowires [74]. Via using a thermal annealing treatment in vacuum/air, the insulating layer induced by the unstable –OH layer on as fabricated ZnO nanowire surface is efficiently eliminated. Such a simple and low-cost method can enhance nanowire atmospheric stability for at least 40 days with stable electrical properties. Meanwhile, Zeng et al. offered a way to overcome the degradation in conventional sensor contact, as shown in Figure 27b [73]. It is found that the nanowire device can obtain good stability for at least over 2000 hours by replacing the easily oxidized contact metal (Ti) with heavily doped metal–oxide (antimony doped tin oxide). Moreover, Yan et al. reported an unusual annealing process on oxide thin films for highly thermal and chemical stability shown in Figure 27c [360,361]. It was indicated that Al-doped ZnO (AZO) nano-thin films could efficiently suppress the inevitable crystal defect formation in the as-fabricated thin film via sequential annealing process under air and Zn vapor atmosphere, resulting in a stable electrical resistivity (~10^{-4} \ \Omega \cdot \text{cm}) in air, even at high temperature (up to 500 °C). This thermally stable thin film can be utilized as electrodes for gas sensors, which obtain stable performance over 250 hours compared to the conventional Ti/Pt contact sensor. Meanwhile, the sequential annealed AZO nano-thin films also show highly chemical stability in buffer solution (pH: 3~11) compared with non-annealed AZO nano-thin films and ZnO thin films. These proposed strategies can successfully suppress the electrical performance degradation of the nanowire devices and have a great potential to be applied to various oxide nanostructures, which would give a foundation for the designing and fabrication of oxide nanomaterial-based IoT sensors with long-term stability.

![Figure 27. (a) Atmospherically stable ZnO nanowires via using the annealing process. Reprinted from reference [74] with permission from the American Chemical Society; (b) gas sensor with long-term stability via using heavily doped oxide as the contact. ATO, Sb-doped SnO$_2$. Reprinted from reference [73] with permission from the American Chemical Society; (c) Al-doped ZnO thin film with thermal stability via using sequential annealing. Reprinted from reference [360] with permission from the American Chemical Society.](image-url)
With regard to the low power consumption, Meng et al. recently reported an excellent thermal management approach in metal–oxide nanowire sensors via a pulsed self-Joule-heating technique, as shown in Figure 28 [220]. It was found that the thermal conductivity of the device was reduced due to the prohibition of heat dissipation from nanowire to surroundings, and its thermal relaxation times can be decreased down to a microsecond range, while several tens of seconds are needed for conventional MEMS gas sensors. This method enables the reduction in energy consumption down to $\sim 10^2$ pJ/s and the enhancement of sensitivity for electrical sensing of NO$_2$ (100 ppb). This proposed thermal management concept of nanowires in both spatial and time domains offers a strategy for exploring novel functionalities of nanowire-based sensors with high performance.

![Figure 28](image_url)

**Figure 28.** (a) Suspended nanowire device; and (b) comparison between the conventional external heating device and pulsed self-Joule-heating device. Reprinted from reference [220] with permission from the American Chemical Society.

With the improvement of the metal–oxide nanowire synthesis and device fabrication processes with high uniformity, the integrated nanowire sensor electronics would have a high reproducibility, selectivity, and long-term stability. This would promote the nanowire sensor electronics to be widely used in the IoT applications, such as medicine, food industry, security, and environment protection.

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