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Nanowire-Based Sensor Electronics for Chemical and Biological Applications

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Detection and recognition of chemical and biological species via sensor electronics is important not only for various sensing applications but also fundamental science understandings. In the past two decades, sensor devices using by one–dimensional (1D) nanowires have emerged as promising and powerful platforms for electrical detection of chemical species and biologically-relevant molecules due to their superior sensing performance, long-term stability, and ultra-low power consumption. This paper will give a comprehensive overview of the recent progress and achievements in 1D nanowire synthesis, working principles of nanowire-based sensors, and the applications of nanowire-based sensor electronics in the chemical and biological analytes detection and recognition. In addition, some critical issues that hinder the practical application of the 1D nanowire–based sensor electronics, including device reproducibility and selectivity, stability, and power consumption, will be highlighted. Finally, challenges, perspectives and opportunities for developing advancement and innovative nanowire-based sensor electronics in chemical and biological applications are featured.

1. Introduction

For the upcoming "trillion sensor electronics" era, molecular sensor and electronic recognition devices, which collect enormous information as big data from various chemical species (e.g. volatile organic molecules, small molecules and ions) and biologically-relevant molecules (e.g. DNA and mRNA, proteins, metabolites, drugs, etc.), have attracted considerable attention due to their promising applications in environment monitoring,[1–5] industrial production,[6–10] food security,[11,12] life health and biomedicine[13–16]. The central to realizing the molecular detection and recognition is the transduction of chemical and biological binding events into electronic and digital signals with a selective merit.[17] To significantly and selectively amplify the molecule binding events, several sensing approaches have been discovered for the detection of chemical and biological molecules, mainly including chemiresistive[18–23], electrochemical[24–28] and Field-effect transistors (FETs)[29–31] types of molecular sensing mechanisms. In particular, with the advancement of nanomaterial fabrication technology, a large number of functional nanostructures, such as nanodots[32–36], nanowires,[37–40] nanosheets,[41,42] and hierarchical nanostructures,[43–45] are synthesized as building blocks for the fabrication of sensor electronics.

Among recent nanostructured forms, one–dimensional (1D) nanowires offer lots of advantages for molecular sensing compared with other nanostructures, which can be summarized as superior sensing performance, long-term stability, and low power consumption. Due to the nanoscale diameter and high surface to volume ratio, very few molecules binding on the nanowire surface is capable of triggering the fluctuation of its electrical properties.[46,47] This allows the nanowire based sensor electronics are able to detect the molecules with high sensitivity and fast response/recovery dynamics,[48–50] and further enables the sensors to work at room temperature, thereby reducing the power consumption.[48,51,52] In addition, the high crystallinity of the nanowire structure would contribute to the improvement of thermal stability and therefore, the long-term working stability of the sensor device.[53] Especially, as the sensor devices are manufactured by single nanowire, it would extremely eliminate the sensing performance degradation that originating from the interaction and mass transfer on the sintering necks and grain boundaries during the high temperature operation.[54,55] Besides, single nanowire device structure enable the utilization of self-Joule-heating becomes possible, which would significantly reduce the power consumed by the sensor electronics.[56–58]

Ever since the first report of using the 1D metallic nanowires as the molecular sensor by Tao and co-workers in 2000[59], great progress has been achieved in the past two decades.[60–66] To date, thousands of papers have been published on sensors integration based on 1D nanowires, including metallic, semiconductor and conducting polymer compositions, for chemical and biological analytes detection, as shown in **Figure 1**. Meanwhile, to fulfil the rising demands of versatile molecule detection and monitoring, many innovative sensor designs have been introduced for the nanowire sensor fabrication and platform integration. For example, chemiresistive sensors that integrated by metallic nanowire networks are fabricated for the detection of hydrogen gas and biological molecules (e.g. Enzyme and glucose, etc.).[67–69] Semiconductor nanowires are used to the fabrication of single nanowire chemiresistive/FET sensor devices the for detection of gas molecule and charged species (e.g. toxic heavy metal cations, DNA, RNA, virus, etc.)[70–

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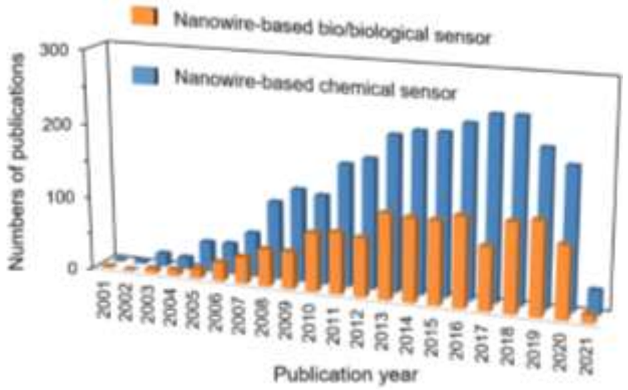

Figure. 1. Numbers of publications in the area of nanowires and nanowire sensors from 2001 to 2021 (internet search of the Web of Science on Apr. 15, 2021). Keywords for search: Nanowire + Chemical sensor; Nanowire + Bio/Biological sensor.

[74]. Electrochemical analysis methods, in which the 1D nanowire structures are integrated as the transduction element (working electrode), also have attracted great interest in the detection of chemical analytes (such as heavy ions) and biological molecules in liquid phase.[39,75–79] In addition, some on-chip sensing systems are designed and fabricated by Si nanowires for proteins separation and recognition.[80] Electronically conducting polymer nanowires, which also attracted the attention of analytical chemists for the fascinating gas sensor and biosensor discovery.[63,81–83] Therefore, molecular sensor and electronic recognition devices design and fabrication derived from 1D nanowires have a bright future in the Internet of Things (IoT) applications.

Here, in this review, we firstly give a comprehensive overview of the recent studies and achievements in 1D nanowire synthesis, working principles of nanowire-based sensors, and the applications of nanowire-based sensor electronics in the chemical and biological molecules detection and recognition. Then, some critical issues that hinder the practical application of the 1D 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. Synthesis of 1D nanowire structures

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 metallic, semiconductor and electrically conducting polymer nanowires.[22,84–89] Generally, the formation of 1D nanowires can be categorized into two paradigms, the top-down and bottom-up approaches (**Figure 2**). In the case of top-down approach (**Figure 2(a)**), nanowires are usually fabricated in well-defined locations with a homogeneous diameter and length, which are realized via a combination of patterning lithography, etching and deposition processes.[90–94] On the contrary, the bottom-up approach (**Figure 2(b)**) starts with single atoms or molecules and self-assemble to 1D nanostructure with high aspect ratio.[93,95–97] Additionally, this nanowire synthesis strategy can realize the nanowire controlling with tunable size, composition, heterostructure, and electronic properties, which directly benefits a lot of distinct nanowire sensor device integration.[98–101] In the past two decades, great effort has been devoted to the discovery and growth of 1D nanowires based on the bottom-up approach.[22,58,99,102–126] In this section, we review

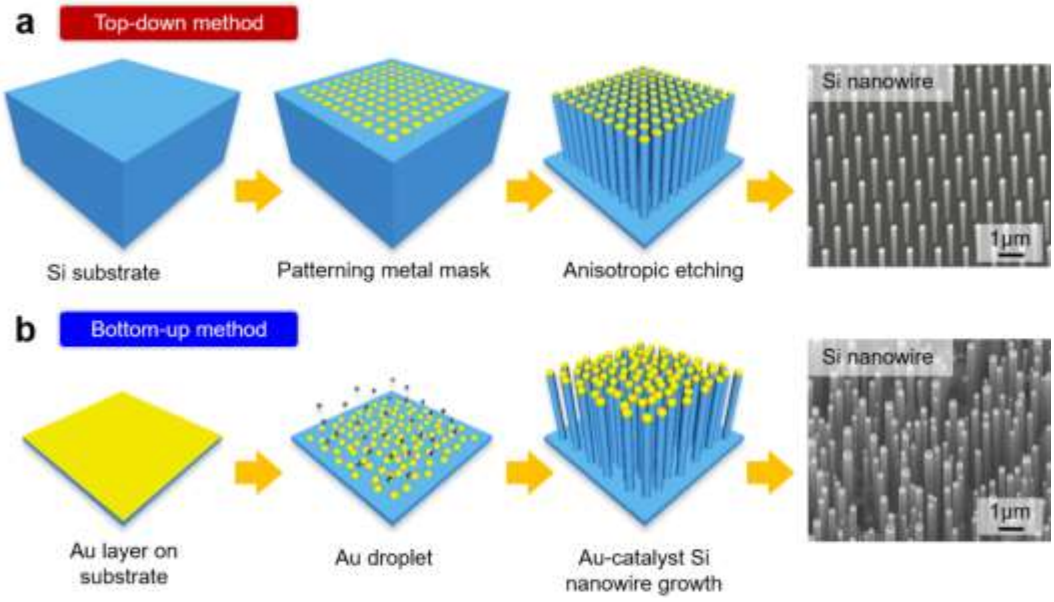

Figure. 2. (a) Top-down method of nanowire synthesis. SEM image is reproduced from ref. 94 with permission from BioMed Central, copyright 2021. (b) Bottom-up method of nanowire synthesis. SEM image is reproduced from ref. 97 with permission from Springer Nature, copyright 2016.

recent progress in the 1D nanowire synthesis in terms of these two paradigms, including homogeneous nanowires and nanowire heterostructures within axial and lateral dimension.

2.1. Metallic nanowires (MNWs) synthesis

MNWs have been explored as sensing elements because they possess an apparent electrical signal fluctuation as analytes binding on their surface.[127,128] To date, various kinds of MNWs, such as single metals (Ag, Au, Pt, Pd, Ni)[60,64,66,74,129–152], bimetallic alloys (NiCo)[153,154] and trimetallic alloys (PtPdCu)[154], are successfully synthesized for the molecular sensing. And their synthesis methods can be classified into three categories: template-assisted electrodeposition[155], self-assembled growth in solution-phase and vapour-phase[156] and lithographically patterned deposition via top-down approach[157,158]. Specifically, the synthetic methods and molecular sensing applications of MNWs in the past two decades have been summarized in Table 1.

Table 1. Summary of metallic nanowire (MNW) synthesis and their molecular sensing applications.

Class	Materials	Analytes	Synthetic method
Single metals	Ag	NH_3[159,160]; NO_2[160,161]; H_2O[160]; H_2O_2[162–165]; 4-nitrophenol[166,167]; Phosphate[168]; Heavy ions[169]	Solvothermal method[161–163,165–168]; Electrodeposition[164]; Drop-casted[159]; LPNE technique[160]
	Au	pH[170,171]; Na^+ [170]; K^+[170]; Heavy ions[74]; H_2O_2[149,172–174]; Dopamine[175]; Cholesterol[147,176]; thrombin[177]; Telomerase[178]	Hydrothermal method[172]; Solvothermal method[149,170,173,174]; Electrodeposition[171,177]; Electroplating[147,176]; CVD[178]; Vapor transport method[74]; LPNE technique[175]
	Ni	Glucose[148]; Glutamate[152]; Salmonella typhimurium[179]	Electrodeposition[148,152]; Solvothermal method[179]
	Pb	H_2[180]	Template-assisted method[180]
	Mo	H_2[181]	Electrodeposition[181]
	Pt	H_2[150]; Glucose[182]; H_2O_2[183]	LPNE technique [150]; Template-assisted method[182]; Electrodeposition[183]
	Pd	H_2[184–190]	LPNE technique[184,185,188–190]; Vapor transport method[186]; Template-assisted method[187]
	Cu	Nitrite[191]	Template galvanic deposition[191]
Bimetallic alloys	NiPt	H_2O_2[192]	Mild dealloying[192]
	AuCu	H_2O_2[193]	Solvothermal method[193]
	NiCo	Glucose[153]	CVD[153]
	AgCu	H_2O_2[194]	Co-precipitation[194]
	AgAu	HNO_3[66]; Rhodamine 6G[195]	Template-assisted method[66]; Thermal deposition[196]
	PtAg	H_2[197]	LPNE technique[197]
	PbPt	H_2[198]; Glucose[199,200]	LPNE technique[198]; Template-assisted method[199,200]
	Pt Au	H_2O_2[201,202]	Template-assisted method[201]; Chemical deposition[202]
Trimetallic alloys	PtCoIr	Procalcitonin[203]	Solvothermal method[203]
	AuCdTe	DNA Molecules[204]	Electrochemical deposition[204]

Template-assisted synthesis coupled with electrodeposition is a facile and efficient strategy to fabricate MNWs structure with uniform diameter and length on arbitrary substrates[205–208]. Recently, anodic aluminum oxides (AAO) are usually applied as hard template for the MNWs growth. For example, Cho et al. fabricated high density and uniform Pd nanowire arrays by utilizing AAO template and integrated such structure as sensor for H_2 detection (**Figure 3(a)**).[209] Cu et al. also used AAO template to successfully fabricated three-dimensional (3D) Pt nanowire arrays and applied them as electrochemical sensors for glucose detection.[136] Besides, polycarbonates, which served as a soft template, are also favorable in the metallic nanowire formation.[210] Hasan et al. demonstrated a convenient way to fabricate Pd nanoparticles modified Au nanowire array electrodes by using polycarbonate membrane templates for H_2O_2 detection.[211] Escarpa et al. also utilized polycarbonate template for the fabrication of Ni and Co metallic nanowires and applied them for the electrochemical detection of carbohydrates involved in metabolic rare diseases.[212] While template-assisted electrodeposition methods sometimes suffering from the difficulty in template removal for some systems.[213]

Self-assembled growth in solution-phase, especially in the polyol process, is a preferred method for the large-scale MNWs synthesis.[214,215] All solution-phase synthesis of MNWs are similar in growth recipes, which usually contain two important reactants, a reducing agent and a capping agent,[216] as shown in **Figure 3(b)**. The reducing agent is an indispensable component during the growth, because it would promote the reducing of the metal ions to metal.

And the capping agent has a structure-directing feature, which preferentially cap a specific crystal face to obtain the selectivity of crystal growth direction.[215] This type of synthesis generally yields MNWs with a typical diameter ranging from 20 to 150 nm and lengths from few to several tens of micrometers.[156] For instance, Huang et al. synthesized graphene/Au nanowire composites via a solvothermal method and applied them as electrochemical gene sensor for tulobuterol detection.[217] Herein, the triisopropylsilane was used as reducing agent and oleylamine served as structure-directing agent. Pu et al. also realized Pt@Pd nanowires synthesis in a mixed solution of ethylene glycol and *N*,*N*-dimethylformamide. It is indicated that Pt@Pd nanowires modified with horseradish peroxidase show an excellent sensing properties toward *Mycoplasma pneumonia* DNA.[218] In addition, Du et al. have demonstrated a bimetallic PtNi nanowire synthesis via a facile solvothermal method for caffeic acid electrochemical detection.[219] Besides, reduction of metal salts in vapor-phase is another feasible way to self-assemble single crystalline metal and metal alloy nanowires.[220,221] Scott et al. have demonstrated a facile method to synthesis Co, Ni, NiCo, CoFe, and NiFe nanowires in nitrogen atmosphere via directly reducing their metal nitride precursors at 550-600 °C.[221]

The significant advancements in the field of lithography have promote the wide application of these techniques in patterned nanowires fabrication with well-controlled placement and feature-size.[222–224] In contrast to the template-assisted MNWs synthesis, in which the metal components are electrodeposited into the nanoporous along the axis of the template membrane and the as-fabricated MNWs are oriented perpendicular to the plane of the membrane after their removal, the MNWs are commonly are obtained horizontally onto the substrate surface,[197] as shown in **Figure 3(c)**. Over the past two decades, several type of pattern synthesis techniques, including optical and X-ray lithography, electron-beam and ion-beam lithography, printing and imprinting and scanning probe lithography, are proposed to the MNWs deposition.[138,184,197,225–229] Prajapati et al. successfully realized the individual Pt nanowire device fabrication with suspended structure through the combination of electron-beam lithography (EBL) and

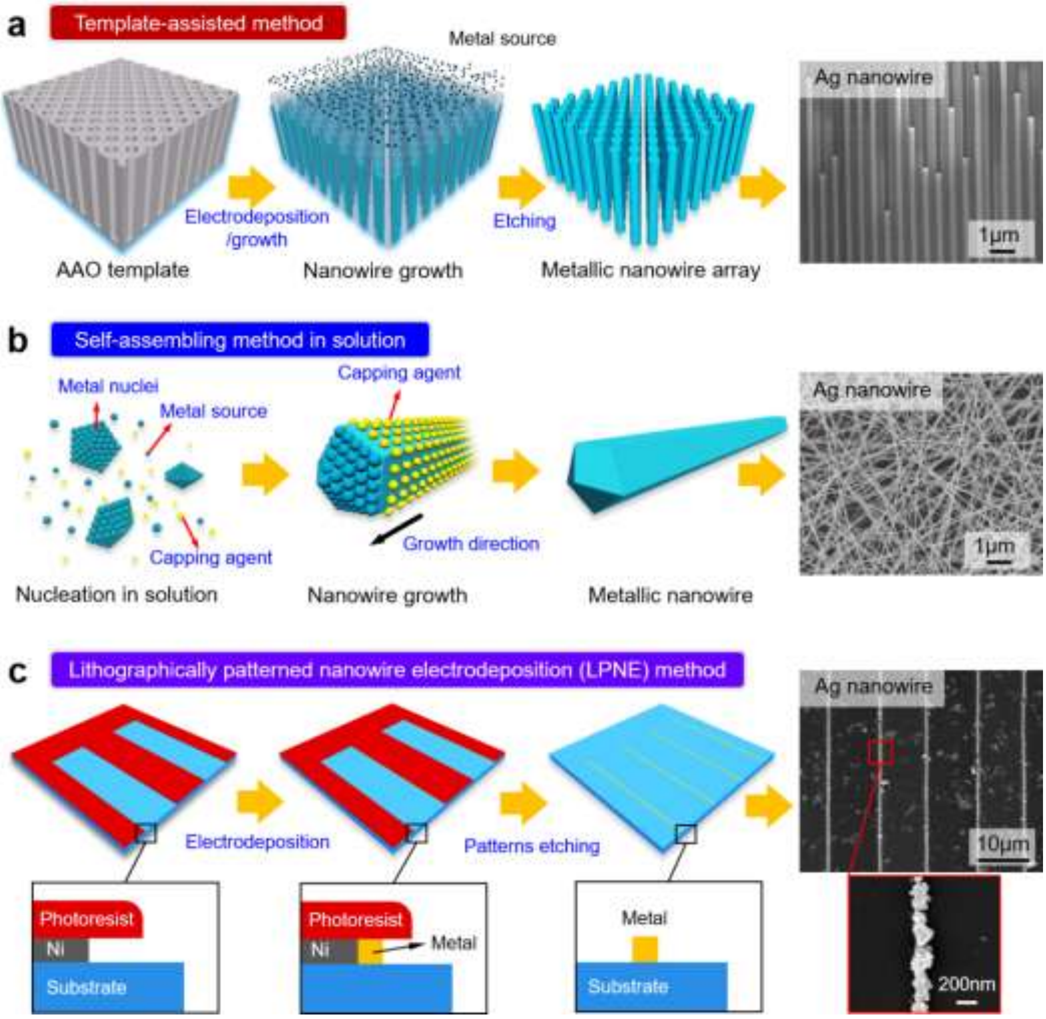

Figure. 3. (a) Template-assisted method of metal nanowire synthesis. SEM image is reproduced from ref. 209 with permission from American Chemical Society, copyright 2003. (b) Metal nanowire self-assembling in solution phase. SEM image is reproduced from ref. 216 with permission from Wiley-VCH, copyright 2016. (c) Lithographically patterned nanowire electrodeposition (LPNE) method of metal nanowire synthesis. SEM image reproduced from ref. 197 with permission from American Chemical Society, copyright 2017.

reactive ion etching (RIE) techniques, and this kind of sensor device enable the sub-ppm H_2 detection with a 500 ppb limit of detection (LOD).[138] Penner et al. demonstrated a nanocrystalline Pd nanowires (with a diameter of 5nm) synthesis through a lithographically patterned nanowire electrodeposition (LPNE), and successfully integrated them as chemiresistive sensor for H_2 detection.[184] Although advanced lithography techniques enable the nanowire fabrication with desired regime in micro/nanoscale dimensions, high equipment cost and complex in fabrication process impede their widely application in large scale nanowire formation.

2.2. Semiconductor nanowires (SNWs) synthesis

Among various nanowire sensing component, 1D SNWs are the most successful and promising candidate for molecule electrical detection due to their high sensitivity and fast response.[230,231] Ever since the first report of using 1D boron-doped silicon nanowires (SiNWs) as molecule sensors for biological and chemical species detection by Cui et al.[232], great progress both on the SNWs synthesis and sensor applications has been achieved in the past two decades.[37,233–235] Up to date, the synthesis of SNWs nanowire are generally categorized as vapor-phase growth, solution-phase growth and template synthesis.[236,237] Here, we will focus the discussion of nanowire synthesis on several important SNWs that corresponding to group IV, group III-V, group II-VI and metal oxide compounds. Similar as the MNWs, the synthetic methods and molecular sensing applications of SNWs in the past two decades have been summarized in Table 2.

2.2.1. Group IV SNWs synthesis

Si nanowire is one of the most important semiconductor nanostructures in group IV, and extensive efforts have been devoted to the synthesis of Si nanowires with controlling structure, doping and electronic structures.[238–240] Recently, numerous methods have been developed to fabricate Si nanowires, which can be generally classified as vapor-liquid-solid (VLS) processed bottom-up approaches and chemical etching assisted top-down approaches.[239–246] Si nanowire VLS growth is a nanocluster-mediated crystal self-assemble process.[240,241,247] The specific growth mechanisms are depicted in **Figure 4 (a)**. Metallic catalyst nanoclusters, such as Au, are firstly ablated by laser or high temperature. As the Si vapor sources (e.g. SiH_4 and Si_2H_6) are fed up to the metallic catalyst at an elevated temperature, a liquid metal/Si eutectic alloy is formed. Subsequently, with the further accumulation and decomposition of Si vapor source at the vapor-liquid interface, the alloy reaches to a supersaturated state and silicon starts to precipitate and forming a liquid-solid interface. Furthermore, with the continuously proceeding of vapor Si source adsorbing at vapor-liquid interface and then transferring to the liquid-solid interface, the Si nanowires are anisotropically grown below the metal nanoclusters.[247] Germanium (Ge) and silicon carbide (SiC) nanowires are another two promising semiconductor nanowire in group IV.[248–251] And they are also can be well grown via nanocluster-catalyzed VLS process. Based on the VLS growth mechanism, well-defined *p*-type and *n*-type Si nanowires are obtained and successfully integrated as electronic sensor devices for the detection of biological and chemical species.[252–256] Lieber's group firstly demonstrated that the boron-doped silicon nanowire (*p*-type) integrated FET device can be used for ions (H^+, Ca^{2+}) and protein (streptavidin) detection.[232] In addition, Lieber's group further confirmed that Si nanowire FET device also can serve as high performance sensor electronics to electrically detect single virus particles.[257] Apart from the ions and biological molecules detection, Haick et al. have proved that molecularly modified SiNW FET device allows the highly accurate detection of volatile organic compounds (VOCs) in both single-component and multicomponent mixtures.[258]

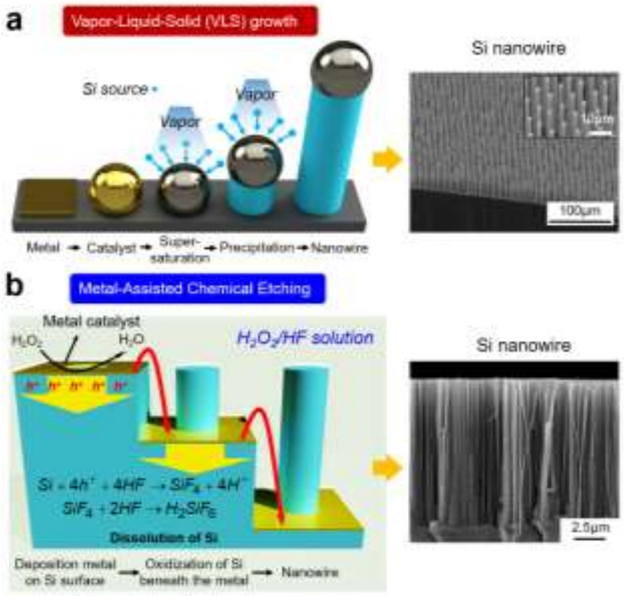

Figure. 4. (a) Typical vapor–liquid–solid (VLS) growth mechanism of nanowire. SEM image is reproduced from ref. 243 with permission from AIP publication, copyright 2007. (b) Metal-assisted chemical etching methods of silicon nanowires synthesis. SEM image is reproduced from ref. 326 with permission from American Chemical Society, copyright 2014.

In contrast to the harsh conditions for the VLS growth of Si nanowires, chemical etching is a simple and low-cost method to fabricate high crystallinity of Si nanowires within the Si wafer.[243–246] Currently, various etching techniques, mainly including reactive ion etching (RIE), electrochemical etching, and metal-assisted etching, are developed to obtain high density Si nanowires.[244,259,260] Among these approaches, metal-assisted etching has attracted considerable interest due to it enable the Si nanowires fabrication with controllable morphology (e.g. cross-sectional shape, diameter, length, orientation, doping type and doping level), as shown in **Figure 4(b)**. In a typical metal-assisted chemical etching procedure, selected area of the Si wafer is firstly covered by noble metals after film deposition. Then, the Si wafer is subjected to an etchant composed of hydrofluoric acid (HF) and oxidative reagent (H_2O_2). Since the Si beneath the noble metal presents a faster etching rate than that of Si without noble metal coverage, the noble metals sink into the Si substrate vertically and generating orientated pores on the Si wafer. As a result, single crystalline and high oriented Si nanowires are formed. For example, Kim et al. used Au layer as catalyst and successfully realized wafer-scale graphene/Si nanowire array fabrication, and this heterostructure integrated molecular sensor shown a huge (1280%) resistance changes and a fast response/recovery (12/0.15 s) times toward H_2.[261]

In addition, high regularity of Si nanowire array can be obtained as the electron-beam or nanoimprint lithography techniques are utilized to design dot array pattern on the Si wafer.[262–264]

2.2.2. Group III-V and II-VI SNWs synthesis

Similarly, VLS-catalyzed growth is also an encouraging approach for the synthesis of group III-V (e.g. GaN, GaSb, GaAs, InAs and InP) and II-VI (e.g. ZnS, CdS, ZnSe and CdTe) semiconductor nanowires.[265–276] For example, Duan et al. report a laser-ablation technique to synthesis high-quality, single-crystal GaAs, GaP, GaAsP, InAs, InP, InAsP, ZnS, ZnSe, CdS, CdSe semiconductor nanowires by using Au as catalyst.[277] Chen et al. have demonstrated that high-purity and -quality GaN nanowires can be well obtained by using metals (In, Co, Ni, Fe) and alloys (Ni/Co, and Fe/Co) as catalyst via controlled VLS growth.[278] Furthermore, such kind of nanowires can also be synthesized via a catalyst-free molecular beam epitaxy (MBE) growth method, which avoids the unintentional catalyst doping during the nanowire VLS growth.[279] While MBE growth has very strict requirements for the growth parameter (e.g. ultrahigh vacuum and lattice matched growth substrate), which impede its widely application in the versatile SNWs growth.[280,281]

As another important approach to synthesis nanowire in terms of bottom-up strategy, solution synthesis has been widely used for the group III-V and II-VI semiconductor nanowire growth.[282] Korgel et al. proposed a Bi nanocrystal seed solution-liquid-solid (SLS) growth of crystalline high aspect ratio GaP, GaAs, InP, and InAs nanowires in conventional solvents such as trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO), and trioctylamine (TOA) at 320–340 °C.[283] Yan et al. demonstrated a hydrothermal synthesis route for the wurtzite ZnS nanowires preparation with a low-temperature (180 °C) in the presence of ethylenediamine (en).[284] Li et al. presented a simple synthetic route for the production of high-quality CdS, CdSe, CdTe nanowires in different organic solvents.[285] However, because inevitable contamination or doping usually occurred during the nanowires growth in solvent, electronic properties of the solution-grown nanowires are far from that of nanowires grown via vapor-phase. In addition, the synthetic methods and molecular sensing applications of Group III-V and II-VI SNWs in the past two decades have been summarized in Table 2.

Table 2. Summary of Si nanowire, group III-V and II-VI semiconductor nanowires (SNWs) synthesis and their molecular sensing applications

Class	Materials	Analytes	Synthetic method
Single semiconductor	Si	NH_3[232,286–297]; H_2[261,298–304]; O_2[261]; NO/NO_2[263,305–308]; H_2O[309–311]; H_2S[312]; Ethanol[313]; Formaldehyde[314]; 2,4,6-trinitrotoluene (TNT)[9,315]; Nerve agent[316,317]; VOCs[318–324]; H_2O_2[325–329]; Glucose[325,330–333]; pH[334–346]; K^+[347]; Heavy ions[254,348–351]; Hydrazine[352]; Exhaled breath VOCs[353]; DNA/RNA[354–361]; Virus[257,360,362–369]; Protein[370–383]; Tumor cell[384]; Action potentials (APs)[385,386]	VLS[232,288,293,294,299,311,318,319,322,347,353,378,385]; Chemical etching[254,261,286,287,290,296,298,303–310,312–314,326–329,331,332,334,349,352,366]; In-plane solid–liquid–solid (IPSLS)[289]; Top-down Microfabrication technique[263,291,297,300–302,315–317,323,335–338,340,341,343–346,350,354–357,359–361,363,364,368–372,374–377,381–384,386]; Oxide-assisted growth[292,295,325,330,333,348,351]; CVD[9,257,320–322,342,358,362,365,367,373,379,380]; Electrospinning[339]
	Ge	H_2O[387]; pH[388]; DNA[389];	VLS[387]; CVD[388]; Ge-condensation technology[389]
Binary semiconductor	GaAs	Methanol, Toluene[390]	Oxidative chemical vapor deposition (oCVD)[390]
	GaN	Ar, N_2, methane[391–393]; H_2[392,394–400]; H_2O[401]; SO_2[402,403]; NO/NO_2[402,404–409]; CO/CO_2[392]; Alchohol[410]; Aromatic compounds[411]; TNT[412]; DNA[413–416]	VLS[405]; CVD[396–401,406,413–416]; Thermal chemical vapor deposition (TCVD)[394,395,404]; Plasma Enhanced Chemical Vapor Deposition (PECVD)[391–393,408]; Molecular beam epitaxy (MBE)[410–412]; Hydrothermal[409]; Top-down Microfabrication technique[402,403,407]
	InN	H_2[417]; NO_2[418–420]; NH_3[420]	CVD[417,418,420]; MBE[419]
	SiC	H_2[421]; H_2O[422,423]; NH_3[424]; Nitrite[425]; DNA[426]; Reactive oxygen and nitrogen species[427]	Carbothermal reduction[421,425]; CVD[422,423,427]; Electrospinning[424]; VLS[426]
	InAs	H_2O[428,429]; NO/NO_2[429–432]; Ethanol[428]; Acetone[428]; Isopropanol[428]; Acetic acid[433]; pH[434]; Proteins[434]; Cell[435]	TCVD[428]; Metal organic chemical vapor deposition (MOCVD)[429,432]; Low-pressure metalorganic vapor-phase epitaxy (LP-MOVPE)[430,431]; MBE[433–435]
	InP	CO, CH_4[436]; DNA[437]	CVD[436]; Chemical beam epitaxy[437]
	InSb	NO_2[438]	CVD[438]
Ternary semiconductor	$Zn_{1-x}Cd_xS$	Ethanol[439]	Solvothermal method[439]
Quaternary semiconductor	Cu_2CdSnS_4	DNA[440]	Solution deposition[440]

2.2.3. Metal oxide SNWs synthesis

Metal oxide semiconductor nanowires, such as ZnO, SnO_2, WO_3, are another promising class of nanostructures that have been widely studied for molecular sensor electronics[441–443]. In recent decades,

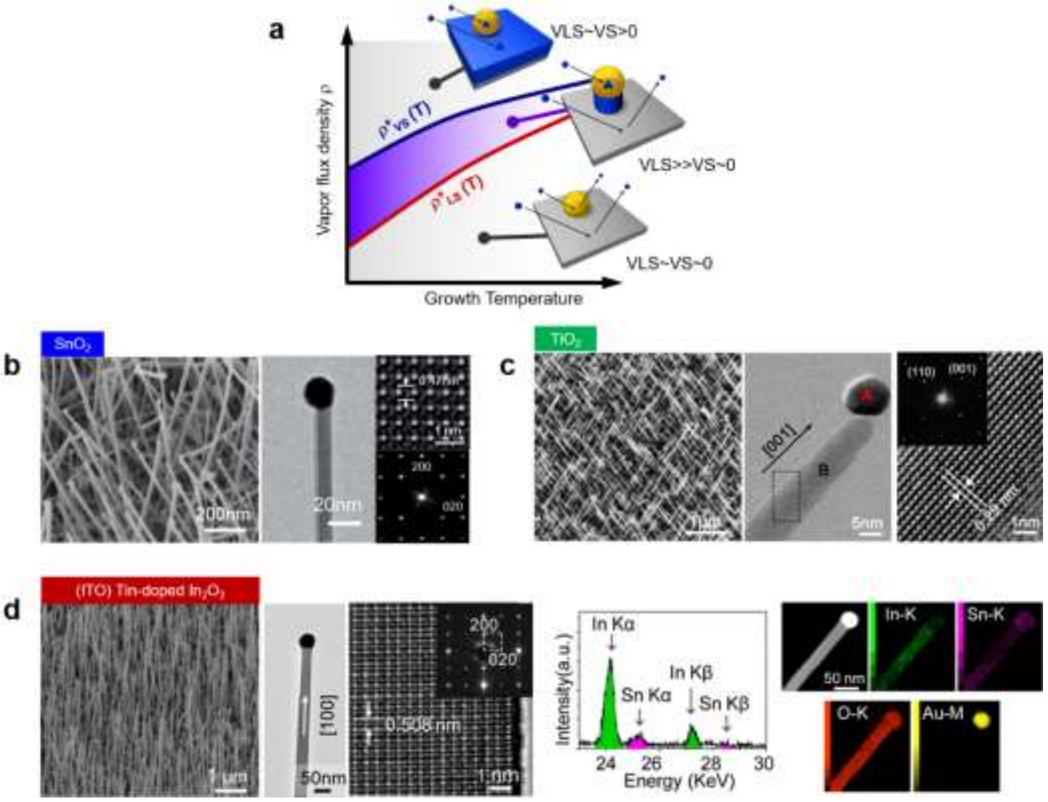

Figure. 5. (a) The concept of "materials flux window" for nanowire growth (VLS, Vapor–Liquid–Solid; VS, Vapor–Solid). Reproduced from ref. 103 with permission from American Chemical Society, copyright 2016. (b) VLS growth of SnO_2 nanowire under the guidance of 'materials flux window'. Reproduced from ref. 103 with permission from American Chemical Society, copyright 2016. (c) VLS growth of ZnO nanowire. Reproduced from ref. 445 with permission from American Chemical Society, copyright 2012. (d) VLS growth of MgO nanowire. Reproduced from ref. 122 with permission from American Chemical Society, copyright 2013.

significant efforts and progress have been made, and many methods have been developed to synthesize 1D metal–oxide SNWs, including PVD, CVD, PLD, thermal oxidization and solution-based growth for single-crystalline nanowires, and template growth, electro-spun for polycrystalline/amorphous nanowires. The synthetic methods and molecular sensing applications of SNWs have been summarized in Table 3. Following with the VLS-catalyzed Si SNWs growth by Lieber group in 1998[444], VLS based growth concept has been intensively applied for the metal oxide nanowire growth. In recent years, the Yanagida et al. has made great efforts in the VLS growth of metal–oxide nanowires[102,103,105,107,112,115,122,445,446]. They have pointed out that materials flux is an important variable which has been underestimated in VLS nanowires growth. In terms of the proposed "material flux window" concept (**Figure 5(a)**), numerous single crystalline nanowires, such as SnO_2, In_2O_3, ITO, ZnO, NiO, MnO, CaO, Sm_2O_3, Eu_2O_3 and MgO, have been successfully synthesized[103,115]. Meanwhile, nanowire heterostructures, which include core/shell heterostructures, axial/radial heterostructures and other irregular heterostructures, can be properly achieved by rationally controlling the growth parameters during the VLS process[116,447]. 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%),[112,122] as shown in **Figure 5(b).**

Owing to the metal oxide SNWs that grown via VLS mechanism have a high surface to volume ratio, single crystallinity, and well-defined crystal orientations, they offer an ideal platform for nanoscale sensor integration due to their high surface to volume ratio, Debye length comparable size, excellent surface chemical reaction, and low power consumption[58,448,449]. For example, Morante et al. successfully realized the grown of single crystalline SnO_2 nanowire by CVD method based on VLS mechanism, and it is indicated that the single SnO_2 nanowire integrated sensor device shown a high sensing response and stability toward CO and humidity[450]. Ho et al. demonstrated a monoclinic β-Ga_2O_3 nanowires growth using the VLS technique along with the Au catalyst, and the

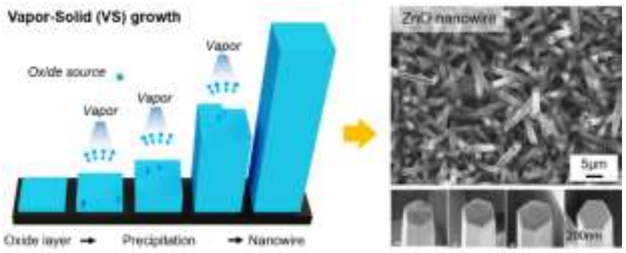

Figure. 6. A typical Vapor–Solid (VS) growth mechanism in nanowire fabrication. SEM image is reproduced from ref. 459 with permission from American Chemical Society, copyright 2015.

single nanowire gas sensor fabricated by the proposed Au decorated β-Ga_2O_3 nanowire achieved remarkable sensitivity for 100 ppm CO gas at room temperature[451].

1D metal oxide SNWs can also be directly formed from the vapor phase into the solid phase, that is, the vapor-solid (VS) growth in the absence of a metal catalyst. Recently, various metal–oxide nanowires, such as Ga_2O_3, ZnO, SnO_2, TiO_2, and WO_3[452–459], have been successfully synthesized via VS growth. 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[460–462]; (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[463–466]; (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, as shown in **Figure 6**. Compared with VLS growth, VS growth nanowires are suffering from insufficient ability to control uniformity, which usually results in a tapered morphology of nanowires.

The solution-phase growth, for example, the hydrothermal growth, is extensively used for the synthesis of metal–oxide nanowires[99,100,106,123,467]. 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. Currently, many kinds of nanowires, such as SnO_2, ZnO, TiO_2, In_2O_3, MnO_2, and WO_3, have been successfully synthesized via solution-phase growth with/without the assistance of the seed layer.[106,468–478] And their growth can be classified as seed-assistant and seed-free growth, as shown in **Figure 7**. 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)[69,479,480]. For example, in terms of the "material flux window" strategy that proposed for nanowire VLS growth, Yanagida research group intensively investigated the seed-assistant ZnO nanowire growth, and they also demonstrated that there existed a "concentration window" in the ZnO nanowire growth. Via carefully controlling the concentration of Zn ionic species within a specific concentration range, a selective growth on the (0001) plane can be realized.[481] Meanwhile, with the guidance of "concentration window" concept, Sakai et al. achieved a significant improvement in the growth rate of ZnO nanowires (up to 2000 nm/h) with the assistance of ammonia.[482] Take WO_3 nanowire growth as an example for the seed-free method, Zhang et al. have successfully fabricated ultra-long *h*-WO_3 nanowires up to the millimeter range (1.2 mm) for a wider range of precursor concentrations through hydrothermal method.[106] They also demonstrated the feasibility of these millimeter-long *h*-WO_3 nanowires for the electrical sensing of molecules (lung cancer biomarker: nonanal) on flexible substrates, which can be operated at room temperature with mechanical flexibility with bending cycles up to 10^4 times due to the enhanced textile effect.

Besides, the thermal oxidation, template-assisted deposition and electro-spinning methods are also developed to synthesize

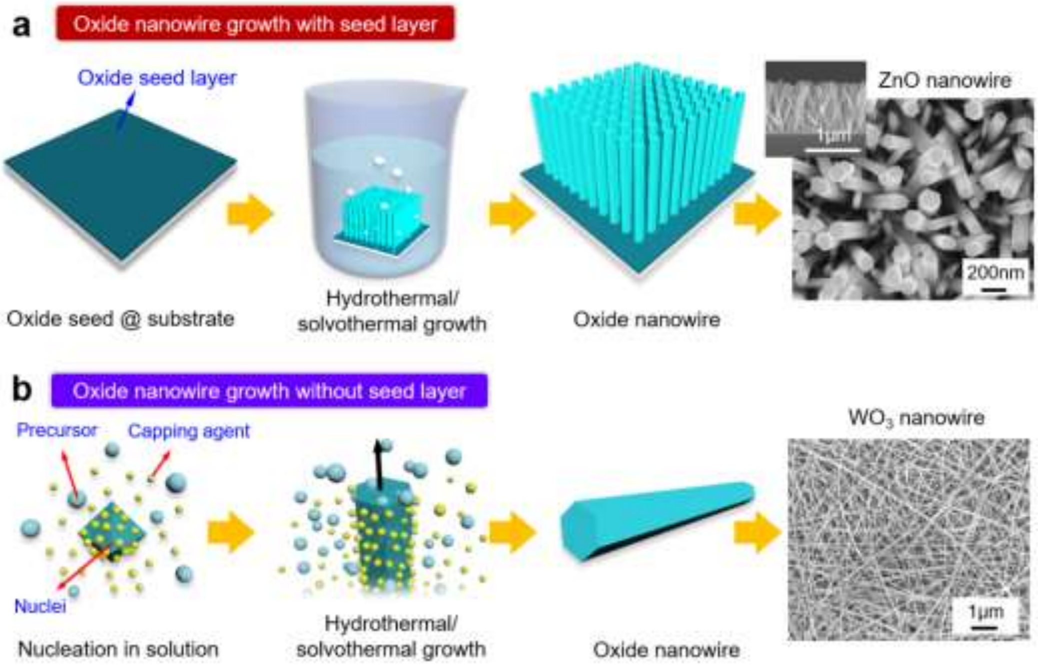

Figure. 7. Hydrothermal/solvothermal growth of metal-oxide semiconductor nanowire (a) with and (b) without seed layer. SEM images of ZnO nanowire is reproduced from ref. 527 with permission from Royal Society of Chemistry, copyright 2021. SEM image of WO_3 nanowire is reproduced from ref. 99 with permission from Royal Society of Chemistry, copyright 2021.

functional metal oxide SNWs,[483–495] as shown in **Figure 8**. For instance, Lee et al. demonstrated a facile method to grown CuO nanowire via a directly thermal oxidization of Cu foil, and it is shown that the CuO nanowire integrated sensor device presented a high sensing performance to 30–100 ppm CO molecules.[493] Hussain et al. reported a template-assisted sol-gel method to fabricate well-aligned 1D ZnO nanowires and applied for CO_2 molecular sensing.[495] Nikfarjam et al. proposed a novel electro-spinning procedure to fabricated single-aligned TiO_2 nanofibers and integrated them sensor to electrically detection CO.[485] Furthermore, electro-spinning technique has attracted increasing attention in the commercial field of molecular sensor fabrication due to its simple and inexpensive fabrication process.

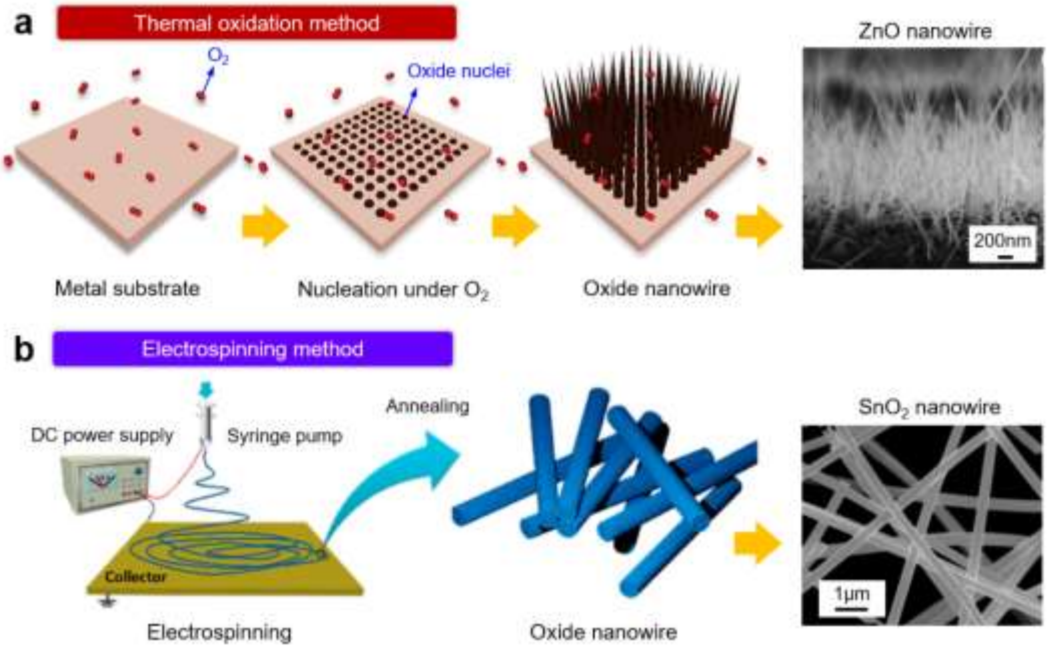

Figure. 8. (a) Thermal oxidization method of metal-oxide semiconductor nanowire. SEM images of ZnO nanowire is reproduced from ref. 491 with permission from American Chemical Society, copyright 2013. (b) Electrospinning method growth of metal-oxide semiconductor nanowire. Reproduced from ref. 494 with permission from American Chemical Society, copyright 2014.

Table 3. Summary of metal oxide semiconductor (MOS) nanowire synthesis and their molecular sensing applications

Class	Materials	Analytes	Synthetic method
Single MOS	ZnO	H_2[48,496–500]; O_2[501]; O_3[502]; CO[498,499,503–506]; NH_3[507–510]; NO/NO_2[108,498,511–515]; H_2S[516,517]; SO_2[518]; Acetone[519]; Ethanol[441,520–522]; Benzene[523,524]; Toluene[523,524]; Formaldehyde[525,526]; Nonanal[527]; K^+[528]; Streptavidin[529]; Uric acid[530–532]; Dopamine[530]; Ascorbic acid[530]; Ammonium[533]; Levodopa[534]; Glucose[535,536]; Hydrazine[537,538]; Protein[539]; DNA[540]	Hydrothermal method[108,499,500,503,508,515,517,518,521,524,525,527,528,531,533,535,538,539]; VLS method[523,529,540]; CVD[48,441,497,498,501,504–506,511,519,520,522,530,532,534,537]; PECVD[526]; Carbothermal reduction[509,510,512,514,516]; Thermal oxidation[513,536]; Evaporation–condensation technique[502]; Template-assisted method[507]; Nanoscale spacer lithography[496]
	SnO_2	H_2[49,234,541–547]; O_2[448,548]; O_3[502]; H_2O[443,549]; CO[234,448,450,541,543,550–553]; NH_3[234,547,554,555]; NO_2[58,234,548,556–567]; H_2S[547,568–571]; SO_2[548]; Cl_2[572]; Ethanol[234,547,550,552,564,573–575]; Acetone[234,576]; Isopropanol[54,550]; Benzene[234]; Toluene[577]; Formaldehyde[578,579]; Liquefied petroleum gas[555]; Cyclodextrin[580]; Methane[551]; Heavy ions[581]; Protein[582]; DNA[583]	Hydrothermal method[569,570]; Polyol method[552,581]; Precipitation method[541]; Spray pyrolysis process[551,566,568]; VLS method[58,546,548,549,556,576,579,580]; VS method[54,450,543,550]; CVD[234,443,547,571,572,574,582]; Thermal evaporation[49,542,544,545,553–555,557–562,564,565,573,575,583]; Evaporation–condensation technique[502,567]; Template-assisted method[448]; Electrospinning[577,578]; LPNE technique[563]
	TiO_2	H_2[584,585]; H_2O[586]; CO[587]; NH_3[588]; Ethanol[589–593]; Methanol[589]; Isopropanol[589]; Toluene[594]; Xylene[594]; pH[595]; H_2O_2[596]; Glucose[597];	Hydrothermal method[586,588,589,594–598,600,601]; Thermal evaporation[584,585]; Sol-gel method[602]; Spray pyrolysis process[590]; Electrospinning[587,592]; LPNE technique[591,593]

		Phospholipid/phosphopeptide[598]; Listeria monocytogenes[599]; Protein[600]; Glutathione[601]; DNA[602]	
	WO_3 /$W_{18}O_{49}$	H_2[442,603–607]; O_3[608]; CO[609]; NH_3[610–615]; NO/NO_2[609,616–619]; H_2S[608,620,621]; Ethanol[622–624]; Acetone[479,625,626]; *n*-Butanol[627,628]; Exhaled breath VOCs[620]; Formaldehyde[622]; Triethylamine[629]; Nonanal[99,100,106]; pH[630]; Rhodamine B[631]; Rhodamine 6 G[632]; Methyl red[632]	Hydrothermal method[99,100,106,479,604,606,610,611,615,619,622,623,625,627,629]; Solvothermal method[605,612–614,628,631]; Electrochemical etching[632]; VLS method[608]; Aerosol-Assisted Chemical Vapor Deposition (AACVD)[620]; Thermal evaporation[442,607,609,620,621,624]; Thermal oxidation[603,616,618]; Electrospinning[626,630]; Nanocasting method[617]
	In_2O_3	H_2[633,634]; O_2[635]; O_3[502]; CO[636,637]; NO_2[471,638]; H_2S[639]; Ethanol[640–642]; Acetone[643–645]; Formaldehyde[646]; SARS virus[647]; RNA[648]; DNA[649]	Hydrothermal method[471]; VLS method[635,636,638,640,644,645,649]; CVD[633,634,636,637,647]; Thermal evaporation[641,643]; Evaporation–condensation technique[502]; Template-assisted method[646]; LPNE technique[648]; Electrospinning[639,642]
	CuO/Cu_2O	H_2[650,651]; H_2O[652]; CO[493,653–656]; NH_3[657,658]; NO_2[659,660]; H_2S[661]; Ethanol[662,663]; Glucose[657,664–671]; H_2O_2[672,673]; DNA[674]	Hydrothermal method[662]; Precipitation method[657]; liquid−solid (LS) growth method[665,668]; Thermal oxidation[493,650,651,653,654,656,658–661,663,664,666,672,674]; CVD[652]; Anodization[667,669–671,673]
	NiO/$Ni(OH)_2$	H_2[675]; NO/NO_2[676,677]; NH_3[678]; Methanol[679]; Ethanol[476,679–682]; Formaldehyde[683]; Acetone[679,680]; Trimethylamine[679]; Toluene[679]; Acetaldehyde[681]; Acetylcholine[681]; Glucose[684]	Hydrothermal method[476,676,679,683]; Chemical reduction[678]; VLS[675,677,680]; Electrodeposition[681]; Nanocasting method[682]; Electrospinning[684]
	Co_3O_4	Acetone[685]; Trimethylamine[686]; Glucose[687]; H_2O_2[688]; Dopamine[689]	Hydrothermal method; Solvothermal method[689]
	Fe_2O_3	CO[690]; H_2S[691]; Ethanol[690,692,693]; Acetone[694]; Glucose[695]	Hydrothermal method[690,692]; Solvothermal method[695]; Thermal oxidation[694]; Nanocasting method[693]; electrospinning[691]
	Ga_2O_3	H_2[696,697]; O_2[698]; CO[451,698–701]; NO[404]; Acetone[404]; Isopropanol[702]; Nitromethane[703]; Trimethylamine[703,704]	Hydrothermal method[699]; Thermal evaporation[696,698,700–702]; VLS[404,451,697,703,704]
	TeO_2	H_2[705]; NO_2[706–709]; NH_3[709]; H_2S[709]; Ethanol[710,711]; Isopropanol[712]; H_2O_2[713]	Thermal evaporation[705,706,708–713]; VLS[707]
	VO_2/VO_x	H_2[714]; NH_3[715]	CVD[714]; Solvothermal method[715]
	CeO_2	H_2O[716]; CO[717]; H_2S[478]; H_2O_2[718]	Hydrothermal method[478,716–718]
	MnO_2	Glucose[719]	Hydrothermal method[719]
Binary MOS	$ZnCo_2O_4$	Formaldehyde[720]; Glucose[721]	Hydrothermal method[720,721]
	$ZnWO_4$	Chloramphenicol[722]	Hydrothermal method[722]
	$ZnFe_2O_4$	H_2S[723]; Acetone[724]	Solvothermal[724]; Electrospinning[723]
	$Na_2Ti_3O_7$	H_2O[725]; H_2O_2[726]	Hydrothermal method[725,726]
Ternary MOS	CuNiCoO4	Glucose[727]	Hydrothermal[727]

2.3. Electrically conducting polymer nanowires (PNWs) synthesis

Ever since the discovery of polyacetylene in the 1970s by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid and co-workers, great efforts are devoted to the developing and synthesis of electrically PNWs for the chemical and biological analytes monitoring and detection. There preparation approaches can be divided into template-assisted method and template-free method.[84,85,728] The synthetic methods and molecular sensing applications of SNWs have been summarized in Table 4.

The template-assisted method was firstly explored by Martin and Parthasarathy who employed aluminum oxide (AAO), commercial track–etch membranes (PTM), porous diblock copolymer films as "hard" template to synthesizing conducting polymer nanowires, such as polyacetylene, polypyrrole, Polythiophene and polyaniline.[729–731] The specific nanowire synthesis processes are shown in **Figure 9(a)**. Within the pores of this templates, electrically conducting PNWs can be obtained by oxidative polymerization of the corresponding monomer via simple chemical oxidization method or electrochemical polymerization.[732–734] Chemical oxidization synthesis is generally accomplished by simply immersing a template membrane in a solution with desired monomer, oxidant and dopant, and then allowing monomer polymerization within the pores.[735] By controlling the polymerization time, different types of nanostructures can be produced.[734–737] For the electrochemical synthesis, a metal film is usually coated on the surface of template membrane, and

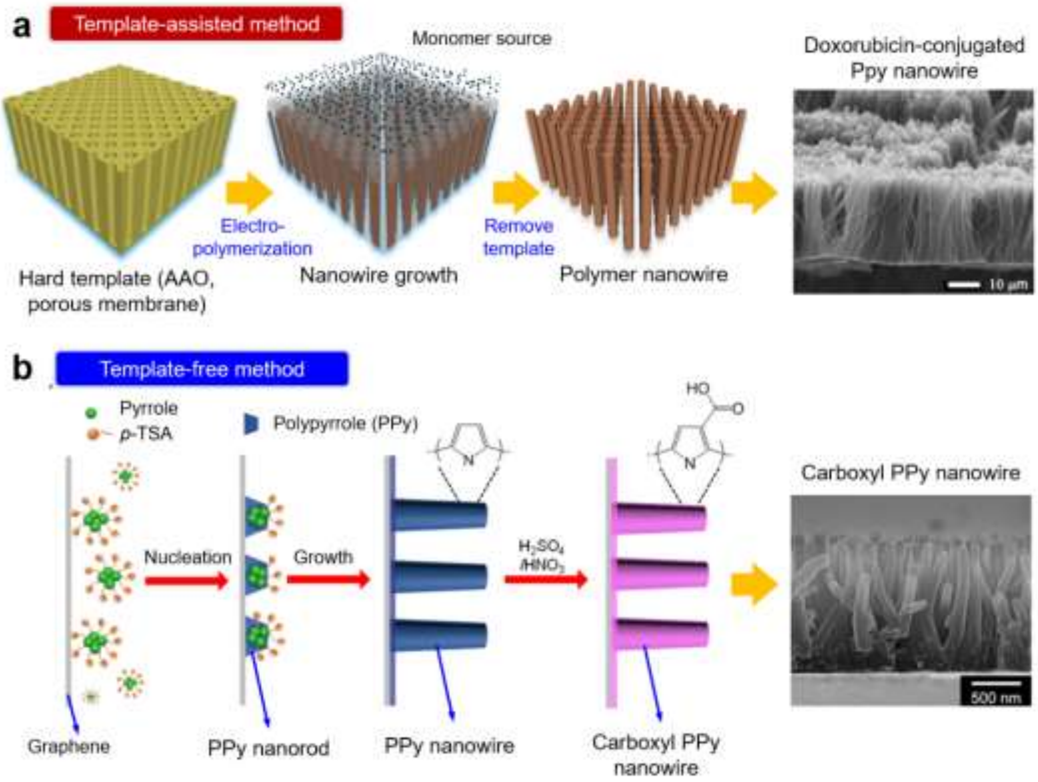

Figure. 9. (a) Template-assisted method of PNWs growth. SEM image is reproduced from ref. 730 with permission from American Chemical Society, copyright 2015. (b) Template-free method of PNWs growth. Reproduced from ref. 744 with permission from American Chemical Society, copyright 2018.

then electrochemical polymerization of the desired polymer within the pores of the template was carried out.[738–740] As compared to chemical oxidization method, the electrochemical polymerization method is more complex and high-cost, but it is more controllable through tailoring current density, applied potential, and polymerization time. Polypyrrole was one of the first conducting polymers to be applied for gas sensing materials.[741] By using $FeCl_3$ as the oxidizing agent, Hernandez et al. realized the chemical polymerization of pyrrole in SiO_2 coated alumina membrane[742]. It is shown that hundreds of nanometer in length and 50 to 60 mm of polypyrrole nanowires can be achieved and the single polypyrrole nanowire integrated sensor device exhibit good sensitivity to 40 ppm of ammonia. Ramanathan et al. demonstrated a simple, one-step method for fabricating single biologically functionalized conducting-polymer (polypyrrole, polyaniline) nanowire on prepatterned electrodes by electrochemical polymerization route in alumina template.[743] And the as-fabricated nanowire sensor generated a rapid change in resistance upon the introduction of biotin-DNA and the limit of detection can be as low as 1 nm.

Template-free method, which is also called as the soft-template or self-assembly method, is another relatively simple, cheap, and powerful approach to synthesize electrical conducting PNWs since it requires no template and no post-treatment for template removal.[744] The specific nanowire synthesis processes are as shown in **Figure 9(b)**. To date, chemical oxidative polymerization, interfacial polymerization and electrochemical deposition have been employed as general template-free methods to assemble conducting PNWs. For example, Pal et al. applied a standard chemical oxidization method to synthesize polyaniline nanowire in the presence of ammonium persulfate as oxidizing agent for the detection of foodborne pathogen, *Bacillus cereus*.[745] Huang et al. reported a facile chemical route to synthesize high-quality polyaniline nanofibers under ambient conditions using aqueous/organic interfacial polymerization.[746] And the polyaniline nanofibers integrated thin film sensor shown a superior performance in both sensitivity and time response to hydrogen acid (HCl) and ammonia (NH_3) gas molecules. Virji et al. also demonstrated an interfacial polymerization method for the synthesis of polyaniline nanofibers and applied them for HCl and NH_3 sensing.[747] Liu et al. realized the fabrication of polyaniline (PANI) nanofibers via electrochemical polymerization approach and used to detect CO contained in hydrogen fuel and volatile sulfur compounds (VSCs) of human expired breath.[748,749]

In addition to above-mentioned template-assisted method and template-free method, other approaches, such as electro-spinning[750], lithographically patterned nanowire electrodeposition (LPNE) process[751], Dip-Pen Nanolithography (DPN)[752] and mechanical stretching[732] have also been used to prepare electrically PNWs for the chemical and biological molecule detection.

Table 4. Summary of Electrically conducting polymer nanowires (PNWs) synthesis and their molecular sensing applications

Class	Materials	Analytes	Synthetic method
Single polymer	Polyaniline (PANI)	H_2[753,754]; H_2O[755]; CO[749]; NH_3[746,747,753,756–759]; NO_2[760]; H_2S[761]; volatile sulfur compounds (VSCs)[748]; Cigarette Smoke[762]; pH[763–765]; Heavy ions[766,767]; Chloramphenicol[768]; H_2O_2[764]; Carcinoembryonic Antigen[769]; Cardiac Biomarkers[770]; Protein[771]; *Bacillus cereus*[745]; DNA[772,773]	Lithographically patterned growth[753,758]; Interfacial polymerization[746,747,760,769]; Electrochemical polymerization[748,749,761,763,765,767,768,770–773]; Template-free method[745,762,764]; Template-assisted method[754,756]; Galvanostatic method[766]; Electrospinning[755,757,759]
	Polypyrrole (PPy)	H_2[774]; NH_3[742,775–777]; pH[190,765,778]; Cu^{2+}[779,780]; Nitrite[781–784]; Glucose[785–787]; H_2O_2[788,789]; CA 125 biomarker[790]; Protein[791]; mRNA[789,792]; DNA[793]	Electrochemical polymerization[81,190,774,776,780–790,792,793]; Chemical oxidative polymerization[779,791]; Template-assisted method[742,765,775,777,778]
	Polythiophene (PT)	Chlorpromazine[794]; Protein[795]	Electrochemical polymerization[794,795]
	Poly(3-hexylthiophene) (P3HT)	NH_3[796]	Liquid-bridge-mediated nanotransfer molding (LB-nTM) process[796]
	poly(3,4-ethylenedioxythiophene) (PEDOT)	H_2O[797]; Methanol[797,798]; Ethanol[797]; Acetone[797]; Fe^{3+}[799]; DNA[800]; Antibody[751]; Nitrite[801]; Protein[802]	Electrochemical polymerization[797,798,800–802]; LPNE technique[751,799]
Copolymer	PEDOT-PSS	NH_3[63]; NO/NO_2[63,752]; *p*-Xylene[62,803]; Acetone[62,803,804]; Methanol[804]; Ethanol[62,804]; Hexane[62]; Isopropamide[62] Streptavidin[81]; Prostate Specific Antigen (PSA)[81]; *Escherichia coli* (*E. coli*)[81]	Electrochemical polymerization[804]; Soft lithography[62,63,803]; Dip pen nanolithography (DPN)[752]

3. Working principles of 1D nanowire-based molecular sensors

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. To date, the molecule sensor electronics can be classified as chemiresistive type, electrochemistry type and field-effect transistor (FET) type of sensor devices based on their electrical measurement strategy.[20,26,29]

3.1. Chemiresistive type of nanowire sensor

The basic principle of chemiresistive sensors is that the chemical interaction between the target molecules with the sensor surface results in electrical conductance variation.[805] In particular, a change in electrical conductance is measured as a function of time for known amount of exposed molecules, and the electric conductance can be measured by a simple ohmmeter. This type of sensor is usually applied for the gas molecule detection and analysis. Chemiresistive molecular sensors based on 1D nanowire are often realized using a single nanowire, a multiple nanowire film or bridged nanowire structures, as shown in **Figure 10**.

Currently, metal oxide semiconductor are the most extensively investigated sensing structures for gas sensing and their sensing mechanisms have been intensively studied.[805] The operation of metal oxide based gas sensors is currently described by two different models, the ionosorption[805] and oxygen vacancy theory model[806]. The ionosorption model considers that the sensor electrical conductivity fluctuation is originating from the space-charge effects/changes of the electric surface potential which result from the "ionosorption" of gaseous molecules. With regard to the oxygen-vacancy model, it explains the sensing effects by changes in the oxygen stoichiometry, that is, by the amount variation of the surface oxygen vacancies and their redox mechanism.

3.1.1 Chemiresistive sensor based on ionosorption model

With regard to the ionosorption model, the key in the mechanistic description of gas sensing is the ionosorbed oxygen ions.[805] Take n-type semiconductor oxide as an example, when a sensor is exposed to the atmosphere, oxygen can be adsorbed on the surface of oxide nanowire and becomes negatively charged ionic species (O_2^-, O^-, and O_2^-). Such oxygen charged

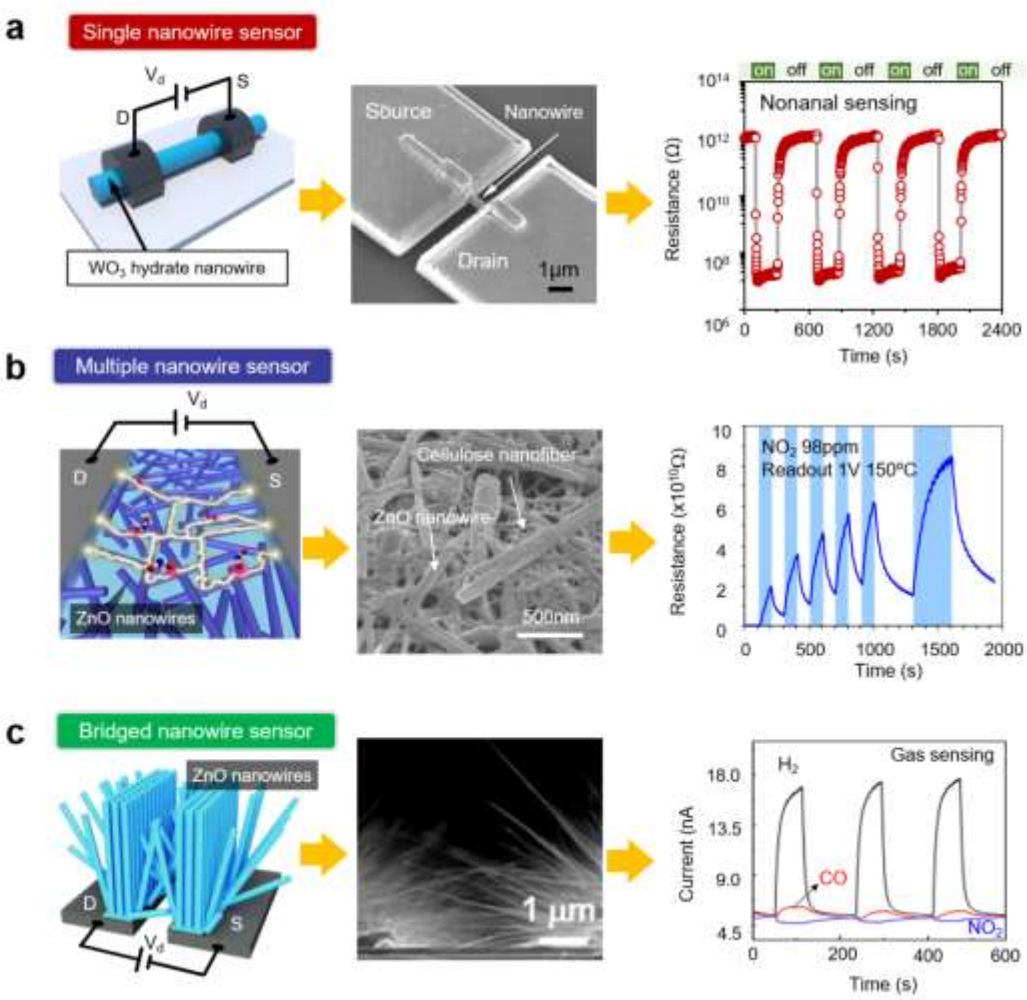

Figure. 10. (a) Single nanowire sensor device for molecular sensing. Reproduced from ref. 99 with permission from Royal Society of Chemistry, copyright 2021. (b) Multiple nanowire film sensor device for molecular sensing. Reproduced from ref. 108 with permission from American Chemical Society, copyright 2019. (c) Bridged nanowire sensor device for molecular sensing. Reproduced from ref. 498 with permission from American Chemical Society, copyright 2013.

behaviour would extract electrons and create a shell-like surface depletion layer on the nanowire surface, which can effectively modulate channel conductivity. As the sensor is exposed to the reducing gases (such as toluene, ethanol, CO, NH_3, H_2, methanol), the charged oxygen 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. In contrast, when the sensor is exposed to the oxidizing gases (such as NO_2, O_3), these gases can extract more electrons from the nanowire surface. Then the depletion layer thickness increases and results in a reduction of nanowire conductance. The detailed working mechanisms are shown in **Figure 11**. Due to its convenience in data analysis, tremendous works have used the Ohmic contacted nanowire device as a platform for fundamental studies to improve the device sensing performance[98,234,776]. The gas sensing mechanism of group IV (such as Si SNWs), group III-V and group II-VI SNWs, and electrically conducting PNWs are similar to the ionosorption sensing mechanism that reported for metal oxide semiconductors.[734,807–809] In the case of n-type semiconductors, the reaction with reducing gases decreases their conductivity, while oxidizing gases increase the conductivity (for p-type semiconductors it is opposite).[810,811]

3.1.2 Chemiresistive sensor based on oxygen-vacancy model

The oxygen-vacancy model focusing on the molecule redox on the surface oxygen vacancy sites, which are considered as the determine factor in the chemiresistive behaviour.[806] Considering n-type semiconductor oxide, for example, the oxygen vacancies (V_O) are the dominated donor defects which are served as active sites for the molecule redox reactions that controlled by the gaseous oxygen. During the alternate reduction and reoxidation of the surface oxygen vacancies between the gaseous oxygen and sensing molecules, the conductivities of the sensing materials are remarkably changes and therefore the overall sensing behaviour. In this model, the mechanism to the reducing gases (R) is represented as follows: 1) reducing gas molecules remove surface lattice oxygen to give oxidation products (RO), thereby producing an oxygen vacancy;

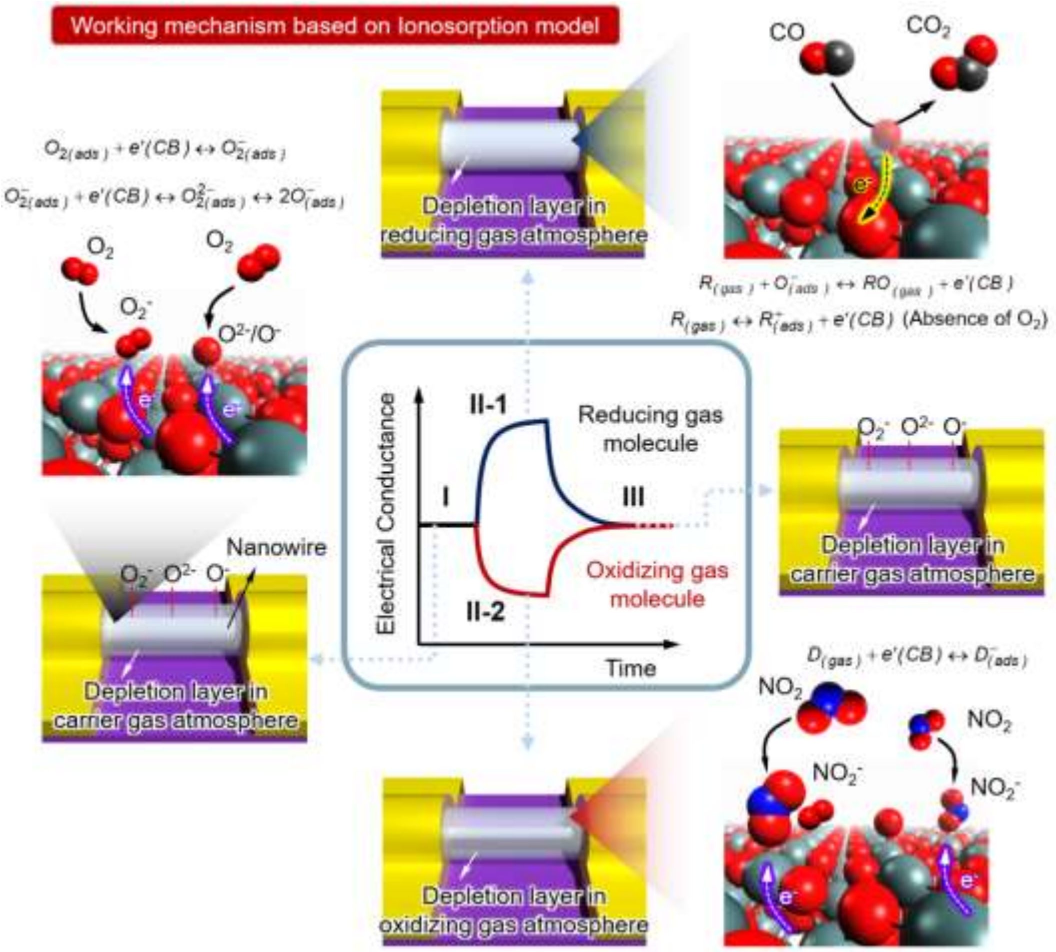

Figure. 11. The detailed working mechanism of the chemiresistive sensor based on ionosorption model. Taking single nanowire sensor device as an example. R: reducing gas; D: oxidizing gas; CB: conduction band.

2) the vacancy becomes ionized at a certain temperature, thereby releasing electrons into the conduction band and increasing the conductivity; 3) in the same time, the oxygen molecules fill the vacancy and trap one or more electrons from the conduction band, which results in the decrease in conductivity. While for the sensing mechanism to the oxidizing gases (D), their electron exchange process on the oxygen vacancy sites are similar as that of gaseous oxygen: 1) introducing of oxidizing gas molecules are directly bonding on the oxygen vacancy sites and trap the electrons from the conduction band, and leading to a decrease of conductivity; 2) as the oxidizing gas molecules desorbed from the oxygen vacancy sites, their trapped electrons are released to the conduction band, which results in the increase of the sensor conductivity. The detailed working mechanisms are shown in **Figure 12**.

3.2. Electrochemistry type of nanowire sensor

Due to the merits of short analytical time, low power cost, high sensitivity and easy adaptability for in-situ measurement, electrochemical detection methods have attracted great interest in the detection of chemical analytes (such as heavy ions) and biological molecules in liquid phase.[26,39,75–77] The electrochemical detection is normally performed with a three-electrode system containing a working electrode (WE), a reference electrode (RE) and a count electrode (CE), as shown in **Figure 13**. The WE serves as the transduction element in the biochemical reaction, while the CE establishes a connection to the electrolytic solution so that a current can be applied to the working electrode.[26] These electrodes should be both conductive and chemically stable. The WE can be modified with different 1D nanowire structures for specific recognition or/and concentration of metal ions.[79] The binding of chemical or biological molecules on the WE causes the change of current, potential, electrochemical impedance, capacitance or electrochemiluminescence, which can then be used for their detection. The working mechanisms of electrochemical sensor are clearly depicted in **Figure 13**. Based on these detection signals, the electrochemical sensing principles can be classified to amperometric[28,812–814], potentiometry[25,27], electrochemical impedance[815–817], capacitance[24] and other methods[818].

3.2.1 Amperometric type of electrochemical sensor

Electrochemical molecular sensing in terms of amperometric measurement is a type sensor that operates under a continuously

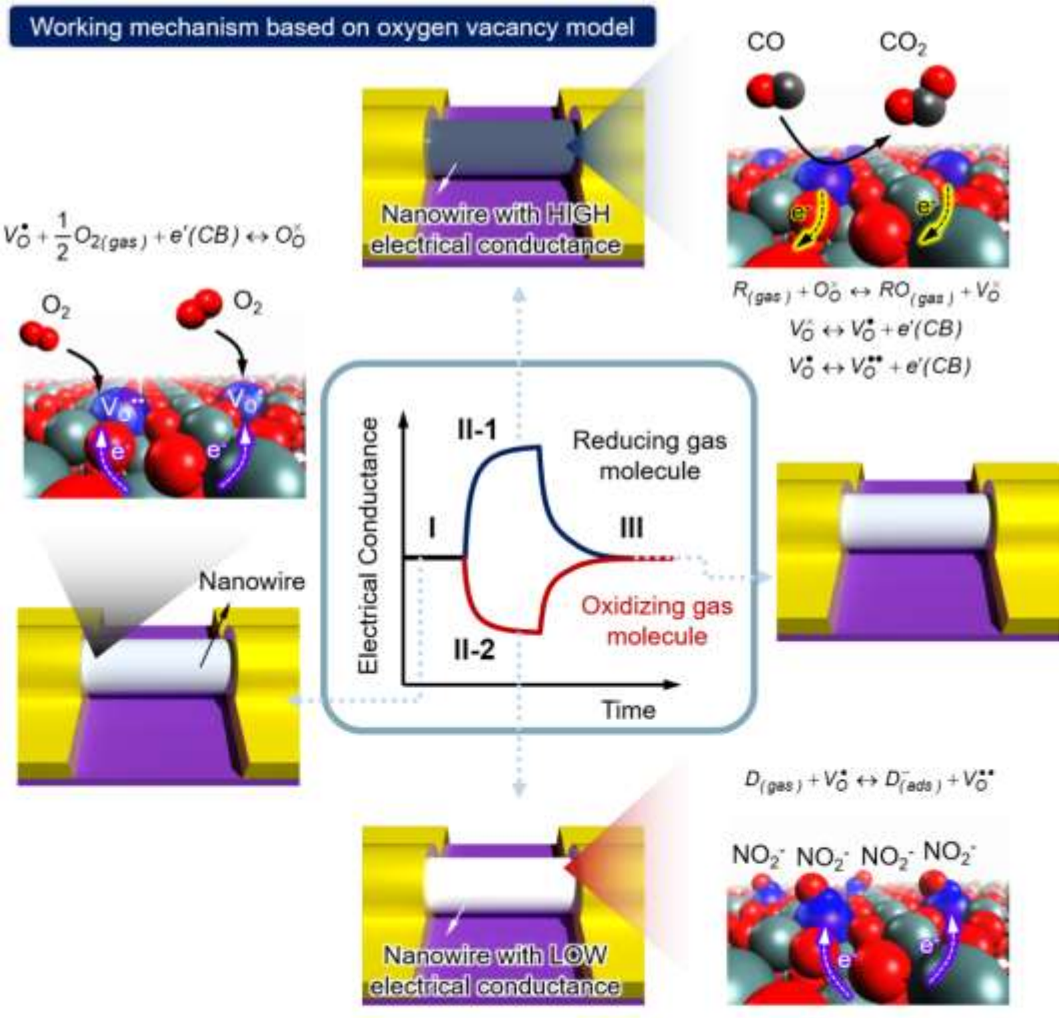

Figure. 12. The detailed working mechanism of the chemiresistive sensor based on oxygen vacancy model. Taking single nanowire device as an example: reducing gas; D: oxidizing gas; V_O^X: oxygen vacancy; $V_O^{\bullet}$: singly ionized oxgen vacancy; $V_O^{\bullet\bullet}$: doubly ionized oxgen vacancy; CB: conduction band.

measure current resulting from the oxidation or reduction of an electroactive species in a chemical/biochemical reaction.[28,812] Typically, the current is measured under a constant potential is referred to as amperometry, and this is similar to the chemiresitive type molecule sensing measurement. Form the view of principle, the peak intensity of the measurement current over a linear potential range is directly proportional to the concentration of the analyte species.[812,819] When a current is measured during controlled variations of the potential, this is referred to as voltammetry. Usually, the electroactive species react on the working electrode have a specific electrochemical cell potential, also known as the redox potential. At the redox potential, ions are adsorbed or desorbed released on the working electrodes which results in electron exchange between the analytes and the electrodes. Electron transfer induces an electrical current flow between the working and the counter electrode in the electrolytic cell system which in turn produces an amperometric response. This sensing response is frequently analysed with a cyclic voltammetric (CV) current peak, as shown in **Figure 14(a)**. Recently, this type of electrochemical sensors are usually applied for the gas molecules[352,537,538,657,715], ions[191,425,782,801] and biological molecules detection[131,135,173,194]. A typical amperometric sensor is the Clark electrode, which is an electrode that measures ambient oxygen concentration in a liquid using a catalytic platinum surface according to the net reaction ($O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$), and it is demonstrated that the produced current is proportional to the oxygen concentration.[820] Furthermore, Kurowska et al. fabricated a novel amperometric sensor based on silver nanowire (Ag NW) array for the a rapid and sensitive detection of hydrogen peroxide (H_2O_2) in the liquid phase, and it is shown that the detection limit of this amperometric sensor can be down to 29.2 μM.[151] Wang et al. demonstrated that the PPy nanowires modified electrode can detect NO_3^- at the micromolar level.[782] A very important application of amperometric biosensor is the detection of glucose. Zhang et al. proposed a highly ordered Ni nanowire arrays integrated electrode for the electrochemical detection of glucose.[148] It is indicated that the as-fabricated nonenzymatic biosensor presented a very high electrochemical activity for electrocatalytic oxidation of glucose in alkaline medium, and a low detection limit of 1×10^{-7} M.

3.2.2 Potentiometric type of electrochemical sensor

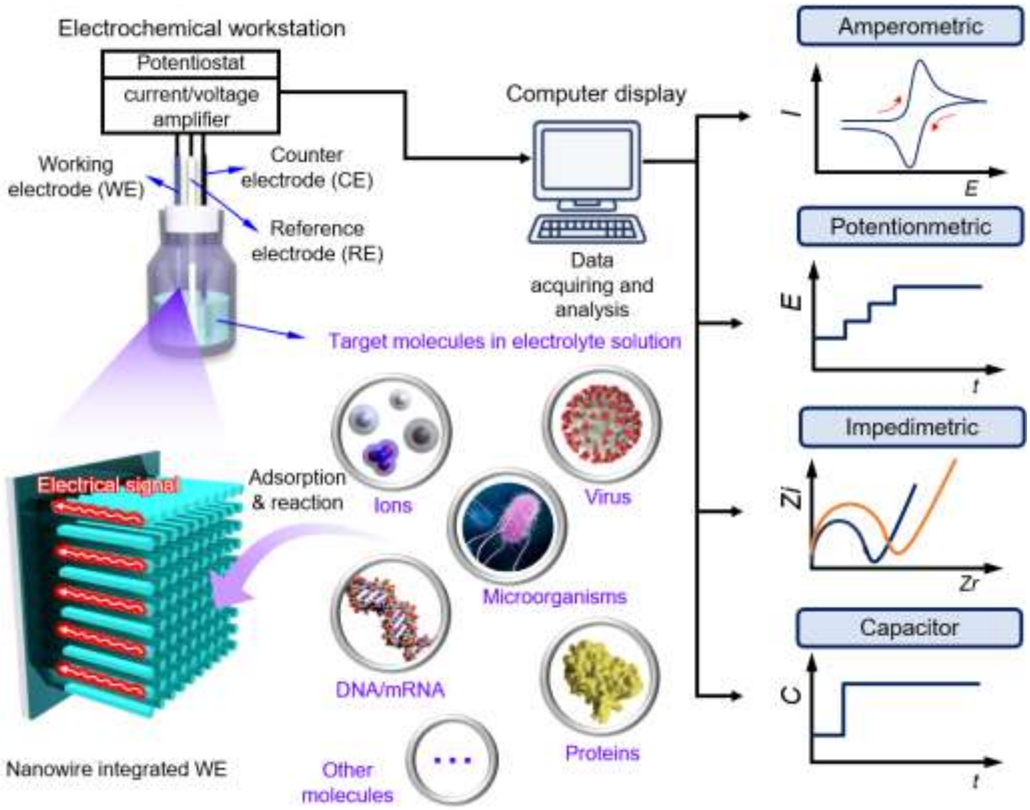

Figure. 13. General setup for electrochemical detection of target molecules and their working mechanisms.

Potentiometric molecule sensing is an important subgroup of electrochemical sensors that generally applied for ions, gas molecules, and biological molecules detection.[821] The largest group among potentiometric sensors is represented by ion-selective electrodes (ISEs), and the most widely used among them is pH sensor electrode.[171,340,342,765] Potentiometric type of electrochemical sensor is performed by measuring the accumulation of a charge potential versus a stable and well-defined reference electrode contacting the sample solution through a liquid junction.[822] For potentiometric measurements, the relationship between the analytes concentration and the potential is governed by the Nernst equation, where E_{cell} represents the observed cell potential at zero current. E^{0}_{Cell} is a constant potential contribution to the cell, R the universal gas constant, T the absolute temperature in degrees Kelvin, n is the charge number of the electrode reaction, F is the Faraday constant and Q is the ratio of ion concentration at the anode to ion concentration at the cathode.[25]

$$EMF\,/\,E_{Cell} = E^{0}_{Cell} - \frac{RT}{nF} ln Q$$

In terms of this working principle, various ion-selective electrodes that fabricated by 1D nanowire are used for the ions and biological molecules detection in the solution.[170,528,531,765] **Figure 14(b)** shows a gold nanowire integrated electrochemical sensor for the potentiometric detection of pH in the solution. Furthermore, recently many potentiometric sensor devices are integrated by combining with various forms of field-effect transistor (FET) devices to measure chemical ions and biological molecules.[823] A conventional ISEs is a two-terminal system wherein the voltage between the working electrode enclosed indicator and reference electrode is modulated by the reaction of ions/biomolecules on the working electrode.[824] While ion-sensitive FETs (ISFETs) employ a three-terminal configuration with an active channel whose current is modulated in the presence of charged species.[823] Owing to the potential for miniaturization, parallel sensing, fast response time, and seamless integration with electronic manufacturing processes, such as complementary metal-oxide semiconductors (CMOS), ISFETs that integrated by 1D nanowire structures have attracted considerable attentions in the chemical and biological molecules detection.[384,532,582]

3.2.3 Electrochemical impedance type of electrochemical sensor

Impedance spectroscopy is a powerful technique of analysing the complex electrical resistance of a system, and it is sensitive to surface phenomena and changes of bulk properties.[815] Thus, impedance techniques are useful to monitor changes in electrical properties arising from molecule binding and interaction events at the surfaces of modified electrodes. Like other electrochemical sensors, impedimetric sensor is a type of electronic devices that make use of the interactions of molecules with an active transducer surface.[361,815,825] **Figure 14(c)** shows a single Si nanowire integrated sensor for the impedimetric detection of protein in the solution. The detection process involves the binding or interaction of the analyte at the interface of the electronic transducer, which directly or indirectly alters the electrical properties of the sensing surface. Impedance spectroscopy is mainly applied in bioanalytics to monitor the biosensor fabrication process, but it is also used to investigate

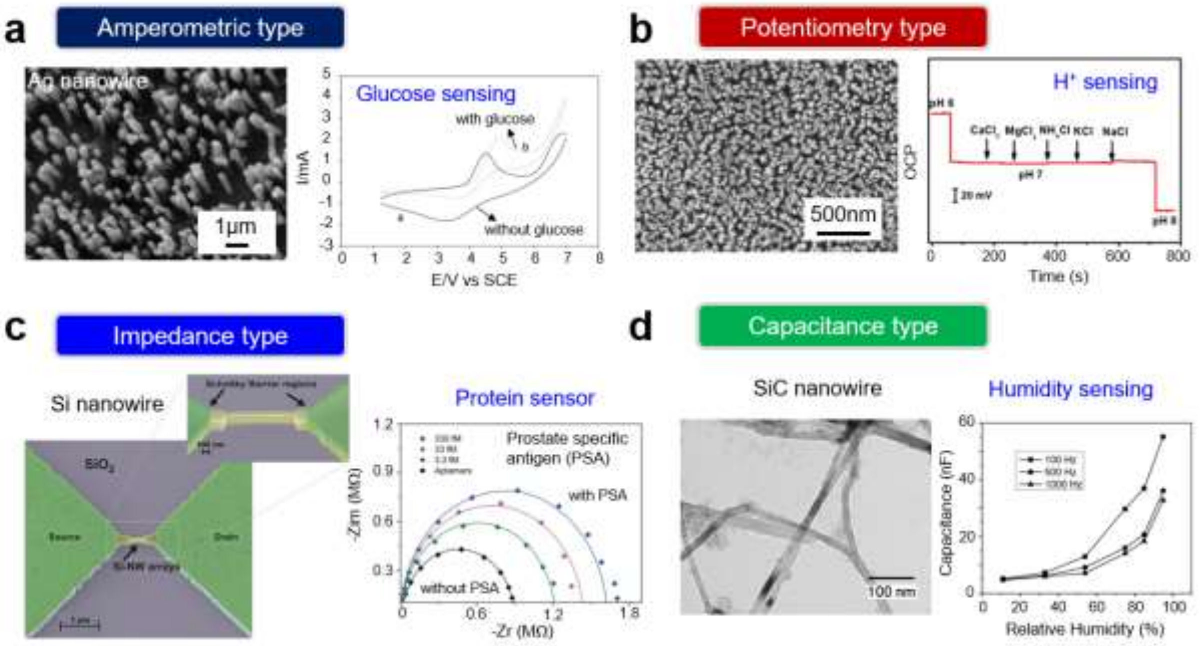

Figure. 14. Typical electrochemical sensor that integrated by nanowire nanostructures. (a) Amperometric type of electrochemical sensor. Reproduced from ref. 148 with permission from Elsevier, copyright 2009. (b) Potentiometry type of electrochemical sensor. Reproduced from ref. 170 with permission from American Chemical Society, copyright 2020. (c) Electrochemical impedance type of electrochemical sensor. Reproduced from ref. 361 with permission from American Chemical Society, copyright 2016. (d) Capacitance type of electrochemical sensor. Reproduced from ref. 422 with permission from Elsevier, copyright 2012.

the recognition process at the biosensor. For example, Lin et al. reported an impedance type of electrochemical sensor for rapid and sensitive detection of *Salmonella* typhimurium by using the aptamer coated interdigitated microelectrode (Nickel nanowire).[179] Huang et al. proposed a novel DNA biosensor based on oxidized graphene and polyaniline nanowires modified glassy carbon electrode.[772] The results indicated that the graphene/polyaniline nanowires showed high selectivity and sensitivity towards complementary DNA sequence.

3.2.4 Capacitance type of electrochemical sensor

Capacitance type of electrochemical sensor is usually referred to a subcategory of impedance sensors, in which the changes in capacitance value are measured indirectly.[24] Capacitive sensor devices are operated based on the changes of the permittivity as the chemical or biological analytes are subdivided into two categories: interdigitated electrodes (IDEs) and electrode–solution interfaces. In the first case interdigitated electrodes are implemented on a substrate and functionalized with probe biomolecules. Reactions then between the immobilized probes and target molecules may be monitored as a change in capacitance or impedance of the device. In the case of electrode–solution interfaces the capacitance variations between a functionalized electrode and a reference electrode into the biological solution are measured. In these systems, the signal is affected not only by changes of the dielectric permittivity of the biological material but also by the increase of its thickness and the displacements of ions and water molecules from the surface. In an alternative approach, capacitance type biosensors and sensor arrays are being developed based on changes of the distance between the capacitor plates. These devices are made of a rigid electrode on the substrate and a flexible electrode, which is typically a membrane.[826] Recently, various 1D nanowires are integrated as capacitive molecular sensor for gas molecules and biological molecules detection.[377,422,535,703] **Figure 14(d)** shows a SiC nanowire integrated sensor for the capacitive humidity sensing.

3.3. Field-Effect Transistor (FET) type of nanowire sensor

FET type of molecular sensors are based on changes in the FET parameters due to the interaction between the channel layer (source and drain) and target molecules.[827–830] Apart from the current variation within the channel, changes in threshold voltage or sub-threshold swing, could also be used for identifying the sensing performance. Recently, many kinds of semiconductor nanowires, such as Si nanowires[254,318,346,369], metal oxides based nanowires (e.g. SnO_2, ZnO and In_2O_3)[532,549,582,636] and electrical conductivity polymer nanowires[743,763,830] have been intensively investigated in FET molecular sensor applications. Nanowire FET molecular sensors work on the principle that adsorption or desorption of molecules on the surface of the nanowire will modify the FET parameters such as channel conductance, which is similar in the sensing mechanism of resistive type of sensors.[29,831] Furthermore, FET-type of molecular sensors are capable to fabricate as chemiresistive and electrochemical type of sensor device, as well as integrate micro-electro-mechanical system (MEMS) with a very small size and a low cost, which have a promising future in the future IoT applications.

Among all the nanowire based FET sensing elements, Si nanowires have proven to be a powerful and versatile tool in the biomedical analytes analysis. In a typical Si nanowire FET device, an electric field is applied via a capacitively coupled gate electrode to modulate the conductivity of the Si nanowire channel, as shown in **Figure 15**. To ensure the device stability, a commonly used reference electrode (e.g., Ag/AgCl, Ag wire, or Pt wire) is used as a solution gate controller and maintained at ground potential to reduce electrical noise.[832] Unlike conventional planar FETs, the sensing performance enhancement of Si nanowire FETs is attributed to the reduced dimensionality and large surface-volume ratio of the nanowire structure, which gives rise to a susceptible response to any perturbation of electric bias that is triggered by the molecule interaction on the surface of the nanowire.[832] Currently, Si nanowire integrated FETs have been employed to convert various bio/chemical charge variations into electrical signals for *in vitro* and *in vivo* applications based on target-receptor binding, such as pH[334,335,337,341,342,346], DNA/RNA[354,356,357,360,833], proteins[370,373,378,380,381,833], and action potentials (APs)[385,386].

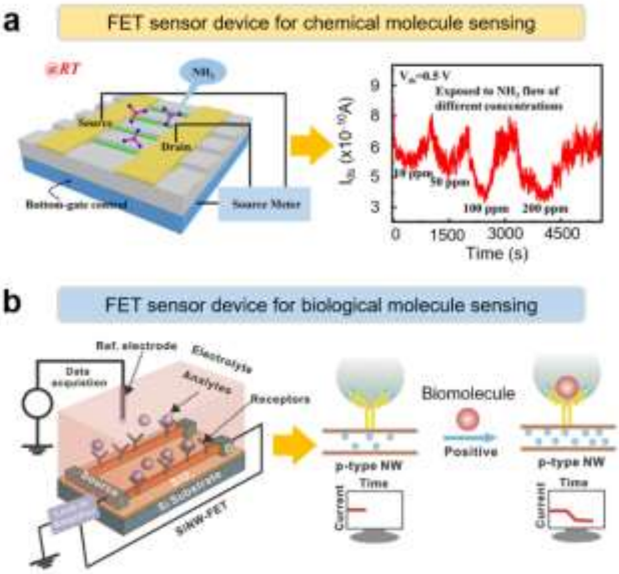

Figure. 15. Schematic illustrations of the FET sensor device for (a) chemical molecule sensing. Reproduced from ref. 289 with permission from American Chemical Society, copyright 2021. (b) FET sensor device for biological molecule sensing. Reproduced from ref. 832 with permission from Wiley-VCH, copyright 2018.

4. 1D nanowire-based sensors for chemical species detection

In this section, we will comprehensively review the recent applications of 1D nanowire based sensor devices for the detection and recognition of chemical species.

4.1. Indoor/outdoor pollutant gas detection

With the rapid development of super smart society, huge achievements are achieved in the past decades, which in turn gigantically improve the daily lives of the human beings. However, unprecedented environmental issues such as indoor and outdoor air quality have accompanied this progress and have triggered public awareness and demands to improve our living standards, especially in residential environments.[834] Poor quality of indoor air may significantly affect an increase in the incidence of various types of human respiratory and related diseases, because people spend most of their time to work and live in the building envelopes.[835] Due to the human activity and emission of building materials, matter and gas pollutants, such as particulate matter, inorganic gases, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), mold, and radioactive compounds, are easy to accumulate indoors.[834] Optical instruments in terms of the detection of light scattering from particles are usually used for the monitoring and detection of indoor particulate matter ($PM_{2.5}$ and PM_{10}).[836] While for volatile gas molecules, lots of electrical conductivity polymer nanowires and numerous semiconductor nanowires, such as Si and metal oxides (**Figure 16(a)**), are synthesized and integrated as chemiresistive type of sensors to realize their detection and alarming.[312,314,448,504,516,523,543,720,749]

As compared with indoor pollutant gases, outdoor air pollution is a more serious health threat to human beings. Due to fossil fuel combustion, burning, industrial/agricultural production, urbanization and traffic transportation, many pollutants such as inorganic gases (eg. SO_2, NO_2, CO, NH_3, CO_2, O_3) and particle matters, are emitted to the living atmosphere.[834] And these pollutant emissions are naturally brought indoors, which results in the worsening of the indoor air quality. Therefore, on the on hand, much effort should be devoted to exploiting renewable energy sources for sustainable development. On the other hand, there is urgent demand to develop simple and reliable methods for detecting and mapping the concentration of toxic and polluting gases.[837,838] Recently, many type of sensors and e-nose platforms that integrated by 1D nanowire structures are developed to acquire and provide the pollutant data in real time[58,98,286,290,291,306,403,405–407,430,438,448,508,512,514,543,557,567,749,839]. **Figure 16(b)** shows a typical SnO_2 bridged nanowire sensor device toward the outdoor pollutant (NO_2) sensing response.

4.2. Humidity detection

Humidity is a natural phenomenon, occurred due to the presence of the moisture contents in the air. It plays a key role in health, manufacturing, storage, and testing processes.[840] Hence, it is essential to develop simple and low-cost sensors capable of accurately quantification the humidity level in the living space and various control systems for industrial and manufacturing processes. In view of the working principles, humidity sensors can be of either capacitive or resistive types.[310,841] The sensing mechanism of capacitive-type of humidity sensors depend largely on the dielectric constant value of the sensing layers, apart from the crucial capacity of the film to enfold water clusters on its surface.[840] Resistive-type of humidity sensors operate through the interaction of water molecules with sensing layer, which directly affect electrical conductivity of the active sensing layer.[805] Among recent sensing elements, metal oxide semiconductor based sensors are promising due to their high sensitivity, fast response speed, long-term stability and repeatability.[842] In terms of the metal oxide, large number of metal oxide nanowire structures (eg.

ZnO, SnO_2 (**Figure 16(c)**), and CeO_2) are synthesized and applied for the humidity detection.[586,652,716,725,843] Besides, electrical conductivity polymer nanowires (eg. PAN) are also considered as a good choice to integrate sensor electronics for humidity detection.[755]

4.3. Food quality and safety monitoring

In addition to the air pollution, food safety is another important public health and challenge issue worldwide.[844] Food quality and safety are of primary importance with respect to nutrition, health, and quality of life. However, chemical and microbiological changes that occur during harvest, transportation, storage and consumption affect food quality and shelf life.[845] As such, monitoring and detection of food pathogens, contaminants such as carcinogens, toxins, and pesticides, that emitted from the food are always necessary. In response to this concern, nanotechnology-based molecular sensors have arisen as a very effective and promising tool due to their high/fast sensing response and low-cost.[845–849] For example, electronic nose (e-nose) instruments have been demonstrated as an effective technique to real-time and noninvasively monitor the quality of muscle food, such as fish, meat and poultry, in terms of the emission of gas/VOCs molecules during their spoilage,[83] as shown in **Figure 16(d)**. Up to now, several electronic noses have already commercially available in the market for the food quality and safety monitoring.[850] And metal oxide

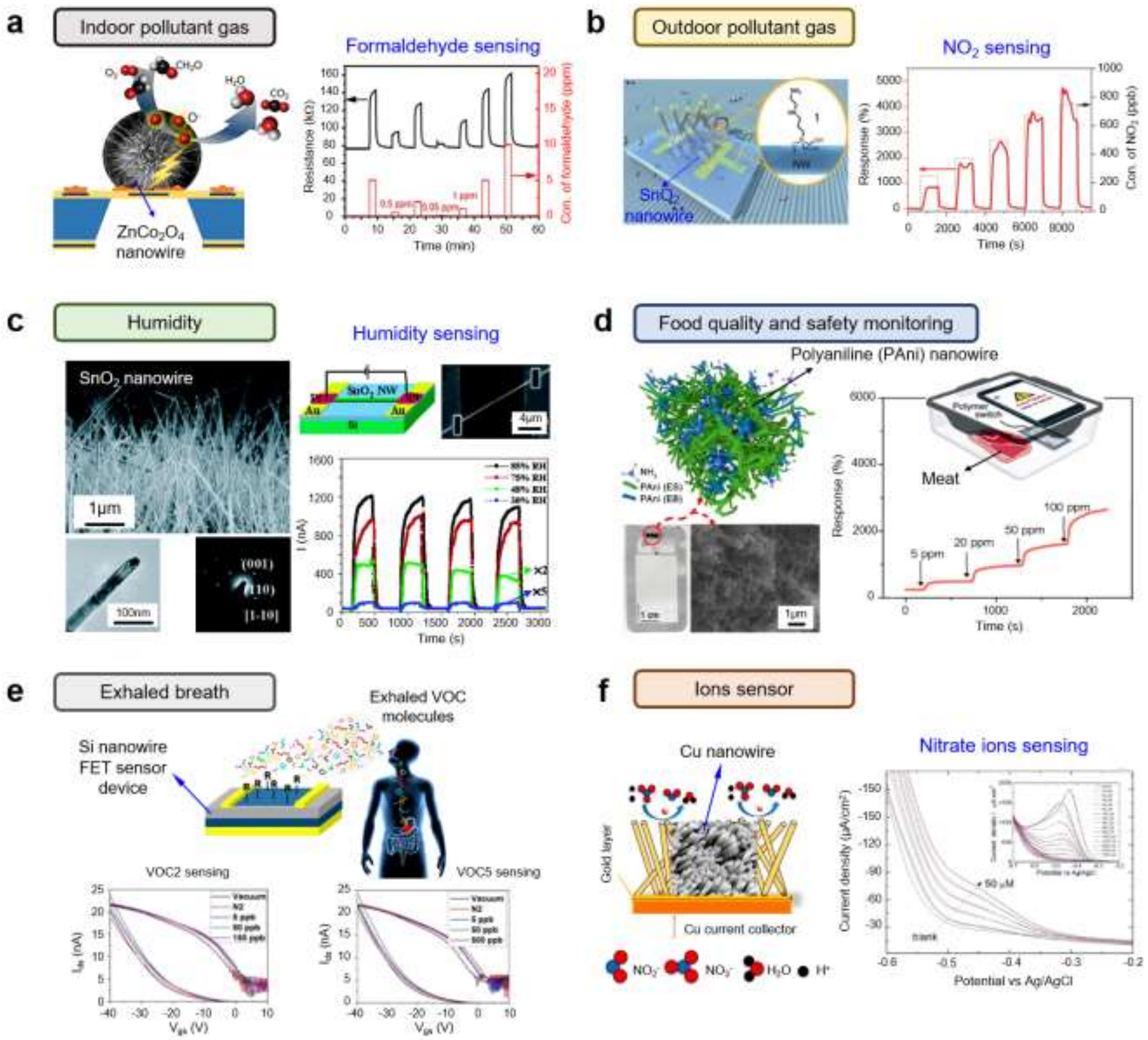

Figure. 16. Nanowire based sensor devices for chemical molecule sensing and detection. (a) Indoor pollutant gas detection. Reproduced from ref. 720 with permission from American Chemical Society, copyright 2016. (b) Outdoor pollutant detection. Reproduced from ref. 567 with permission from Wiley-VCH, copyright 2014. (c) Humidity detection. Reproduced from ref. 443 with permission from American Chemical Society, copyright 2007. (d) Food quality and safety monitoring. Reproduced from ref. 83 with permission from American Chemical Society, copyright 2018. (e) Disease-related VOCs molecule detection from exhaled breath. Reproduced from ref. 353 with permission from American Chemical Society, copyright 2016. (f) Ions detection in solution. Reproduced from ref. 191 with permission from Elsevier, copyright 2021.

semiconductor and electrical conductivity polymer are the most successful sensing elements for the integration of these electronic noses.[10,83,632,745,851]

4.4. Disease-related VOCs molecule detection from exhaled breath

Recently, exhaled breath test based on the detection and classification of the biomarkers, namely the chemical profiles of volatile organic compounds (VOCs) linked with disease conditions, has been considered as a promising method for the disease early detection due to its clinical non-invasive, direct and real-time of merits[852,853]. At present, gas chromatography-mass spectroscopy (GC-MS) and fluorescence spectroscopy (FS) are still the primary options for discriminative molecular analysis, whereas they are expensive, time consuming, and too large to be integrated.[854] Therefore, developing high performance molecular sensing and discrimination platforms, especially to meet the demands for future portable electronic devices, are urgently needed. During the last decade, many efforts have been devoted to exhaled breath analysis by electrically molecular sensors.[353,855–857] Recently, gas sensors based on silicon nanowires, metal oxide nanowires, electrical conductivity polymer nanowires and their composites have been widely reported for exhaled breath analysis and applied for the diseases early diagnosis (**Figure 16(e)**).[99,100,353,620,748]

4.5. Ions detection in solution

Ions, including cations and anions, play a vital role in a broad range of environmental, technological, and physiological processes.[858] Hence, realize the accurate detection/quantification of these ions is essential and valuable. Electrochemical molecular sensing, which offers a strategy to detect the ions with high selective/sensitive, low-cost, portable, and real-time analysis, have received considerable attentions in the past decades.[26,859] As one of the most important application, electrical molecular sensors have widely applied in the heavy metal ions (e.g. As^+, Cd^{2+}, Pb^{2+}, Hg^+ and Cr^{3+}) monitoring and detection.[26,860–864] As is known, heavy metal ions are extremely toxic pollutants which are carcinogens and non-biodegradable, and long-term exposure to them and ubiquitous distribution would lead to a greater risk to human health and environment.[865] Recently, metallic nanowires (e.g. Au, Ag), Si nanowires, metal oxide semiconductor nanowires (e. g. SnO_2, ZnO, WO_3), electrical conductivity nanowires (e.g. PAN) and their compositions have successfully synthesized as sensing electrodes for these ions detection.[74,169,254,348–351,581,766] In addition, proton (H^+) detection, that is pH sensor, are highly demanded in various applications such as chemical reaction, health monitoring, agriculture and food safety, and water quality monitoring.[866] Up to now, a variety of proton measurement techniques, such as conductometric/capacitive[867], potentiometric[868–871] and ion sensitive field effect transistors[337,872,873] are exploited for the monitoring of protons in the solutions. Apart from the cation ions, accurate monitoring the level of anions, such as nitrate (NO_3^-)[191] (**Figure 16(f)**), phosphate (PO_4^{3-})[168] and ammonium (NH_4^+)[533], are also science important in environmental pollution control, food, clinical analyses and other industry.

5. 1D nanowire-based sensors for biological species detection

Apart from the chemical molecule analysis, nanowire integrated sensor electronics also show a promising applications in the biological species (e.g. DNA/mRA, proteins, biomarkers and virus) detection and recognition. In this section, we will comprehensively review the recent applications of 1D nanowire based sensor devices in the biological species detection and recognition.

5.1. Protein biomarker detection

Early disease diagnosis is a crucial and promising research field in human health.[874,875] Recent proteomics and genomics research has revealed that many new protein biomarkers are formed in the bio fluids as human body encounter a specific disease, such as cancers.[874] Hence, biomarker detection and evaluation hold enormous potential for the disease early diagnosis. Recently, 1D nanowire integrated biosensor electronics are emerging as a talented sensing platforms for the biomarker detection due to their ultra-sensitive, low-cost and low-power-consumption.[39,61,78,876] In terms of the working principles, the biomarker sensors can be classified into two categories: label-based and label-free sensors.[877] Label-based sensors use biomarkers that are decorated by secondary labels, such as fluorescent materials, magnetic beads, or even biological materials. Their working principles are as follows: (1) the secondary antibody (Ab2) is decorated with electroactive labels, such as biochemical materials and nanoparticles of novel 1D materials; (2) the Ab2 is bound on the analyte through an intermediate antibody (Ab1) and then is immobilized onto the electrode surface by specific binding; and (3) the concentration of the analyte is obtained by measuring the current at the electrode. Compared to the label-based sensors, label-free electric sensors operate based on the electrical property changes as the biomarkers directly binding on the sensing materials.[878] By measuring these changes, biomarker information, such as concentration, is able to be achieved, which can be applied for the related disease diagnose. Among various electrical transduction sensor electronics, nanowire-based FET structures have been considered as a promising tool for the biomarker detection and reported in many studies.[40,827] For example, Janissen et al. demonstrated an ultrasensitive and highly selective disease biomarker biosensor based on surface functionalized InP nanowire FET sensor device.[437] The developed devices provide ultrahigh label-free detection sensitivities ∼1 fM for specific DNA sequences, measured via the net change in device electrical resistance. Similar levels of ultrasensitive detection of ∼6 fM were achieved for a Chagas Disease protein marker (IBMP8-1), as shown in **Figure 17(a)**. Lieber et al. have reported a highly sensitive and multiplexed detection of cancer marker proteins using Si nanowires.[437] It is shown that the cancer marker antibodies modified Si nanowire arrays allowed the real-time multiplexed detection of free protein specific antigen (f-PSA), PSA-α-antichymotrypsin (PSA-ACT) complex, carcinoembryonic antigen (CEA)and mucin-1 with good signal-to-noise ratios and enabled the limit of detection down to a 50- to 100-fg/mL level. In addition, Si nanowire FET biosensors can also be utilized as the label-free sensor electronics for the protein detection.[437] Apart from Si nanowire, other nanowire structures, such as conductive polymer nanowire[81,770,771,790,791] and semiconductor nanowires[365,370,372,376,437,530,582], are also favorable for the sensor electronics integration for the protein marker detection.

5.2. Virus detection

Viruses are the most common cause of human disease[879], as well as war crisis[880]. For example, as the outbreak of highly contagious SARS-CoV-2 in the end of 2019, 167,011,807 cases have been confirmed as infected, and meanwhile, this pathogenic Coronavirus has causes 3,472,068 deaths up to now.[880] Hence, accurately detect viruses in the early stage will dramatically prevent the pandemic and save lives. Recently, Cell culture-based techniques, mainly including nucleic acid sequence-based amplification (NASBA)[881] and real-time polymerase chain reaction (real-time PCR)[882], are the gold standard for viral detection.[882] Meanwhile, the biosensor techniques have arisen as a promising tool to electrochemical detection the infected viruses due to the high sensitivity and specificity in the past decades.[883] **Figure 17(b)** shows a high selectivity detection of influenza A viruses from clinical exhaled breath condensate (EBC) samples (diluted by 100-fold) within minutes by using silicon nanowire (SiNW) integrated sensor devices[365]. Among various 1D nanowire sensing elements, Si nanowire and metal oxide nanowire sensors which have excellent biocompatibility are broadly explored as novel biological sensor electronics for highly sensitive detection of viruses, such as Dengue[363,364,369], SARS[647], Influenza A H3N2[257,365], H5N2[362], and HIV[368].

5.3. DNA and RNA detection

Deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) detection via advanced biological sensor electronics has enabled many opportunities in modern health for the disease diagnosis/treatment.[358,884,885] Recently, nanowire sensor electronics have been demonstrated as a successful platform for the detection of specific sequences of DNA and RNA.[358,886–888] For example, Ingebrand et al. used a long-channel, ion-sensitive silicon nanowirefield-effect transistor devices (ISFETs) that fabricated in a top-down approach for the DNA capture and detection,[886] as shown in **Figure 17(c)**. Liber et al. demonstrated a p-type Si nanowire resistive sensor for ultrasensitive and

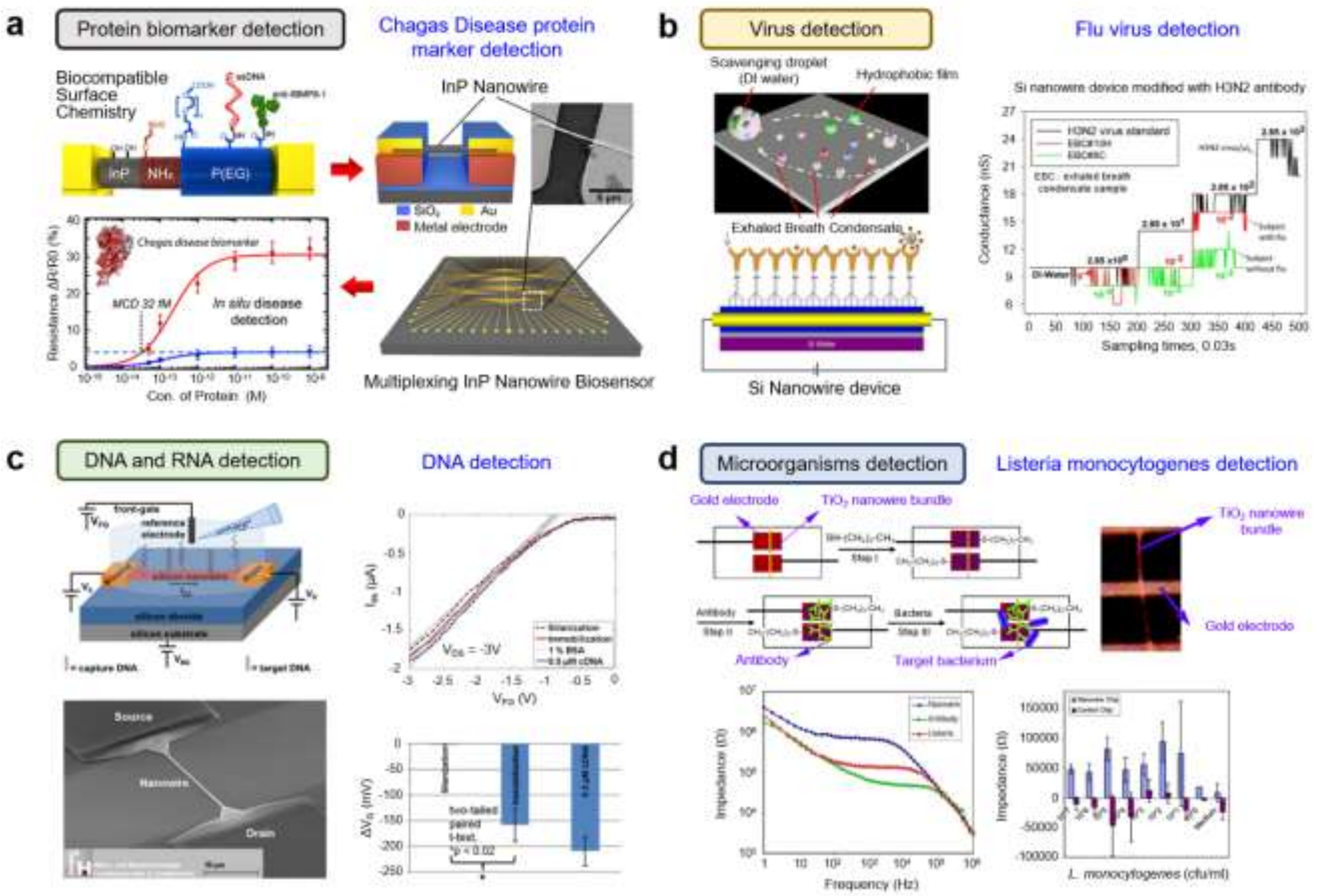

Figure. 17. Nanowire based sensor devices for biological molecule sensing and detection. (a) Protein biomarker molecule detection. Reproduced from ref. 437 with permission from American Chemical Society, copyright 2017. (b) Virus detection. Reproduced from ref. 365 with permission from American Chemical Society, copyright 2012. (c) DNA and RNA detection. Reproduced from ref. 886 with permission from Wiley-VCH, copyright 2016. (d) Microorganisms detection. Reproduced from ref. 599 with permission from American Chemical Society, copyright 2008.

selective real-time DNA sensing.[358] It is shown that the Si nanowire sensors functionalized with peptide nucleic acid (PNA) receptors can distinguish wild-type from the ΔF508 mutation site in the cystic fibrosis transmembrane receptor (CFTR) gene and their detection limit can down to tens of femtomolar range. Wang et al. reported a FET biosensor based on uniformly sized high-response silicon nanowire (SiNW) array for real-time, label-free, super-sensitive detection of PIK3CA E542K ctDNA.[889] In order to recognize the target ctDNA, The Si nanowires were modified with the probe DNA through silanization and acted as a molecular gate and it is indicated that the as-fabricated biosensor had significant superiority in ctDNA detection, which achieved ultralow detection limit of 10 aM and a good linearity under the ctDNA concentration range from 0.1 fM to 100 pM. In addition, Si nanowire devices also served as excellent RNA sensor electronics.[354,355] For instance, Chen et al. reported an ultra-sensitive Si nanowire FET biosensor for the detection of GC-rich RNA.[354] Specifically, Si nanowire FET device was surface functionalized by hepatitis C virus (HCV) genotype 3b chimeric neutralized DNA (nDNA) probe, and it is indicated that the revealed that the HCV-3b chimeric neutralized DNA (nDNA) probe exhibited better performance for SNP discrimination in 10 mM bis-tris propane buffer.

5.4. Microorganisms detection

Every year, millions of people worldwide are infected by the food or waterborne pathogens (e.g. bacteria, viruses, and parasites) via the consumption of contaminated water and food.[354,355] Hence, rapid and accurate detection of hazardous microorganisms in water and food is also of high importance for the public health and environment protection. Current methods of diagnosis these pathogens are based on conventional microbiological culturing techniques followed by biochemical identification.[890] Although accurate infections can be concluded by these techniques, time consuming and labor-intensive have impeded the early diagnose and treatment of these pathogens caused diseases.[891] In recent years, nanowire integrated biosensor electronics have been emerged as a successful tool for the detection of whole bacteria, bacterial byproducts and metabolites, as well as enzymes.[82,179,599,745,892,893] For example, Alocilja et al. developed a direct-charge-transfer (DCT) biosensor that integrated by polyaniline nanowire for the the detection of the foodborne pathogen, *Bacillus cereus*.[745] The biosensor was fabricated using antibodies as the sensing element and polyaniline nanowire as the molecular electrical transducer. The sensing signal was recorded as the resistance change upon the antigen–antibody interaction. Testing of the biosensor showed that it had the ability to detect the presence of the target microorganism, B. cereus, at concentrations as low as 10 CFU/ml, the detection time being only 6 min. Li et al. reported a TiO_2 nanowire bundle-based immunosensor connected with an Au microelectrode for the impedimetric detection of *Listeria monocytogene*s, a foodborne bacterial pathogen,[599] as shown in **Figure 17(d)**. This platform exhibited a high sensitivity, high selectivity (poor response to other foodborne pathogens such as *Escherichia coli O157:H7*, *Salmonella Typhimurium*, and *Staphylococcus aureus*.) and rapid (1 h assay time) detection to the target pathogens, and offered the limit of detection as low as 500 CFU/mL.

5.5. Others

In addition to the detection of various biological macromolecules, nanowire-based sensor electronics have a potential application in drug discovery[894] and electrophysiological signal generation and measurement, such as the measurements of intracellular action potentials generated by beating cardiomyocytes[385,895,896] and extracellular action potentials from brain tissues and cells[897,898], the development of 3D macroporous tissues[899], and the study of the metabolism of cells[900].

6. Critical Issues and Perspectives of Nanowire-based Sensor Electronics

Despite the extraordinary achievements of 1D nanowire-based sensor electronics, there still exists several challenges that need to be overcome to make these devices commercially available for chemical and biological analytes monitoring and recognition. Here, we mainly discuss four remaining critical issues, including reproducibility, selectivity, stability, and energy consumption, and the perspectives against these challenges.

6.1. Reproducibility of devices

Integrating of nanowire device allows us to study the intrinsic properties of the nanowire, as well as to explore the potential sensing applications. However, a tiny variation in the size or shape of nanostructures will powerfully alter their physical/chemical properties and functionalities. Thus, we should carefully consider how to synthesize nanowires with high uniformity. Template-assisted nanowire growth has been considered as 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.[901] Recently, Zhao et al. reported a two-step method to fabricate ZnO nanowires with uniformly shaped structures.[113] 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) of ZnO nanowires are grown in the second step. Such a high uniformity in nanowire diameter would significantly increases the performance reproducibility of nanowire based sensor devices. This unique finding paves the way for the fabrication of nanowires-integrated nanodevices with reliable performance.

6.2. Selectivity of Device

Another critical issue is the selectivity of the sensor device. 1D nanowire sensors generally have high sensitivity to the gas analytes, but they are also suffering from poor selectivity. To enhance the selectivity of gas 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 nanowire-based molecular sensors toward the target molecules. However, the results are usually far from prospects due to the low operational stability. Inspired by the catalytical chemistry, it is worth considering combining porous materials such as zeolites, metal–organic frameworks, and mesostructured oxides with a nanowire.[902–904] Canlas et al. reported a novel method to fabricate molecules imprinted oxide catalyst.[905] 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 nanowire based gas sensor and biological sensor to gigantically improve selectivity due to their preferential interactions with specific VOC molecules and biological macromolecules, even with a chemically similar structure. In addition, biological receptors, e.g. peptide nucleic acid (PNA)[358,906], aptamers[907] and antibodies[908,909], are usually functioned on the nanowire surface to realize the biological analytes or cells specific binding and sensing.

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. However, although numerous efforts are devoted to improving the long-term stability of nanowire sensors, the influence of humidity, poisoning, and contact issues still exist to prevent such a kind of sensors from the practical applications. Thus, preventing the sensor device degradation of nanowire bulk, nanowire/electrode contact and electrodes is the only way to achieve long-term stability of nanowire devices. Recently, Nakamura et al. also demonstrated a strategy for achieving the atmospheric electrical stability of ZnO nanowire device via a sequentially thermal annealing treatment in vacuum/air.[121] This 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 of device contact by deposition of antimony doped tin oxide (ATO) instead of conventional contact metal (Ti).[120] And it is indicated that the nanowire sensor device can work stably over 2000 hours. Besides, Zhou et al. recently introduced a simple method to improve the long-term stability of the Si nanowire FET biosensor devices through surface deposition of Al_2O_3 shell.[910] It is observed that the diameter of the Si nanowire remained almost the same after 100 days of storage in Phosphate-Buffered Saline (pH 7.4) and neurobasal solvent, respectively, while the Si nanowire without the shell was disappeared. These strategies propose some ideas to significantly improve the long-term stability of the nanowires in complex environments, opening up the further investigation of using nanowire as the platform for the harsh environment applications.

6.4. Power consumption

An external heater or power supply is usually needed to drive the efficiency operation of the nanowire-based gas sensor and biological sensor, which inevitably increases the power consumption and sensor size. To effectively decrease the power consumption of the nanowire sensor electronics, several options are proposed, such as (1) developing room temperature sensing materials, (2) using the self-Joule-heat technique and (3) harvesting energy via piezoelectric effect. Meng et al. recently reported an excellent thermal management approach in metal–oxide nanowire sensors via a pulsed self-Joule-heating technique.[58] It is 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.

With the improvement of the 1D 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.

Author contributions

G.Z. and T.Y. wrote this manuscript. All the authors contributed to improve the manuscript, the manuscript preparation and approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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