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Sensors

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Nanowire Chemical/Biological Sensors: Status and a Roadmap for the Future

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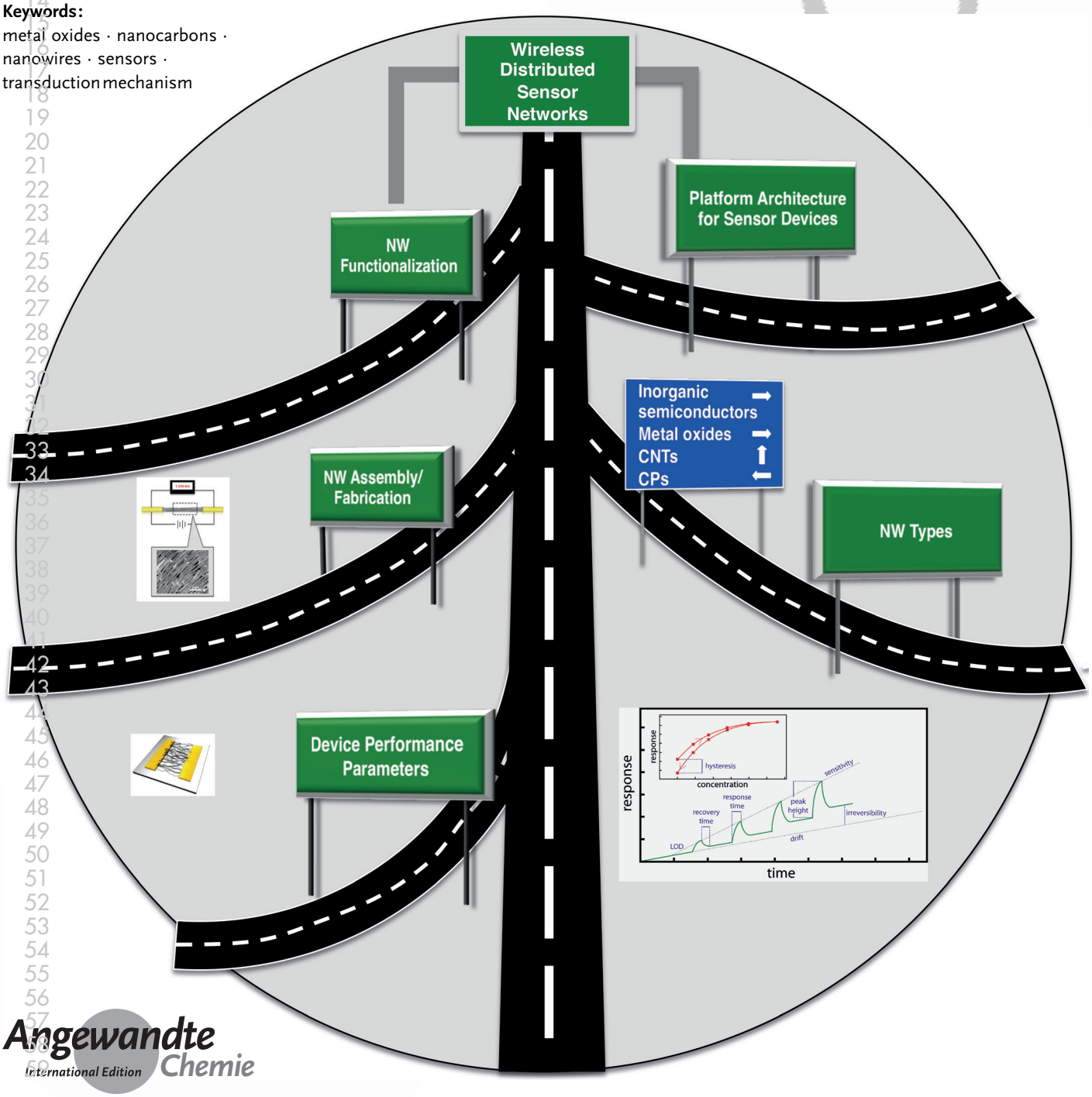

Chemiresistive sensors are becoming increasingly important as they offer an inexpensive option to conventional analytical instrumentation, they can be readily integrated into electronic devices, and they have low power requirements. Nanowires (NWs) are a major theme in chemosensor development. High surface area, interwire junctions, and restricted conduction pathways give intrinsically high sensitivity and new mechanisms to transduce the binding or action of analytes. This Review details the status of NW chemosensors with selected examples from the literature. We begin by proposing a principle for understanding electrical transport and transduction mechanisms in NW sensors. Next, we offer the reader a review of device performance parameters. Then, we consider the different NW types followed by a summary of NW assembly and different device platform architectures. Subsequently, we discuss NW functionalization strategies. Finally, we propose future developments in NW sensing to address selectivity, sensor drift, sensitivity, response analysis, and emerging applications.

From the Contents

1. Introduction

The omnipresence of wireless devices, cloud data, and printable electronics is an extraordinary opportunity for electronic chemical sensors. These sensors enable governments, businesses, and individuals to satisfy an ever-expanding appetite to measure chemical and biological processes as well as physical quantities. Over the last decade, modern electronic chemical sensors have contained nanowires (NWs). The assertion that NWs offer advantages in sensors is often made without justification. However, we contend that it is generally warranted. The simplest reason is their high surface area to volume ratios, which allows more interactions with analytes. However, monolayers of 2D materials such as graphene[1,2] and MoS_2[3–7] also have high surface areas. The most important difference between 1D NWs and 2D materials is how they transport current.

In a NW, electrical transport is primarily along the NW axis. If the NW is small enough in diameter, high sensitivity is achieved because analytes can bind anywhere along the NW to perturb its entire conductivity. This effect is similar to what our group reported with semiconducting polymers, where we demonstrated signal gain by wiring receptors in series.[8] Although this principle was studied for exciton rather than charge transport, there was a correlation between the carrier path length and signal amplification. Thus, long single NWs are attractive because sensitivity increases with the length available for interacting with analytes. However, they are difficult to fabricate.

Alternatively, disordered NW networks can be readily deposited by solid transfer, printing, spraying, or drop-casting a dispersion. Random networks of NWs, as opposed to densely packed aligned networks, have the advantage of porosity with high surface area as well as limited contact between NWs to give restricted pathways that preserve the 1D character. The contacts between NWs are critical: For NWs with high carrier mobilities, these junctions are conductivity-limiting. Various intra- and inter-NW mechanisms of transduction are illustrated for single-walled carbon nanotubes (SWCNTs) in Figure 1. Amongst all the NWs, our group favors SWCNTs because of their excellent conductivity, exceptional aspect ratios, and numerous methods available for functionalization.

For many systems, reductions in conductivity are observed as coherence in electronic transport is destabilized by heterogeneous potentials that result from analytes. However, analytes can also enhance conductivity by facilitating charge transfer across resistive interfaces, lowering barriers, or injecting carriers through doping.

That a "turn-on" response is more sensitive than "turn-off" is often stated in fluorescence; however, this assertion is only true with zero background fluorescence in the absence of analyte and emission only in the presence of analyte. The analogy for NWs is an insulating device that becomes conductive upon exposure to an analyte. If this activation is achieved by carrier injection, high sensitivity is obtained when the NW has very low carrier density in the absence of the analyte. Alternatively, NW networks can be assembled slightly below a percolation threshold such that they are highly resistive, and an analyte-triggered formation of new conduction pathways can produce a large turn-on response.

Sensitivity without selectivity, however, is simply noise. Systems should respond strongly only to desired analytes. Coupling molecular processes to conductivity changes for selectivity often involves careful molecular constructions.

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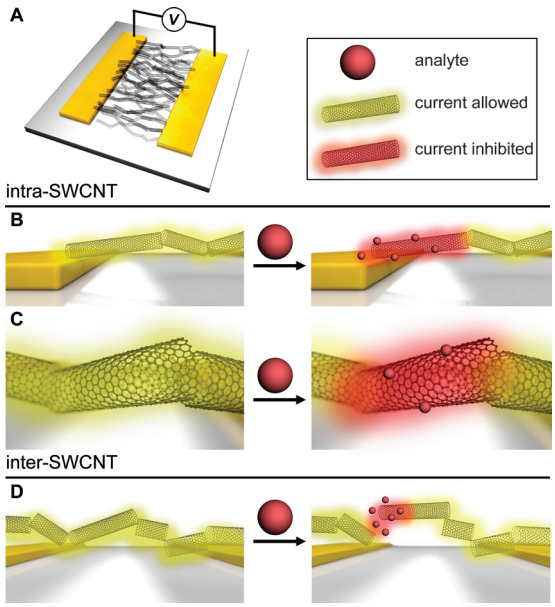
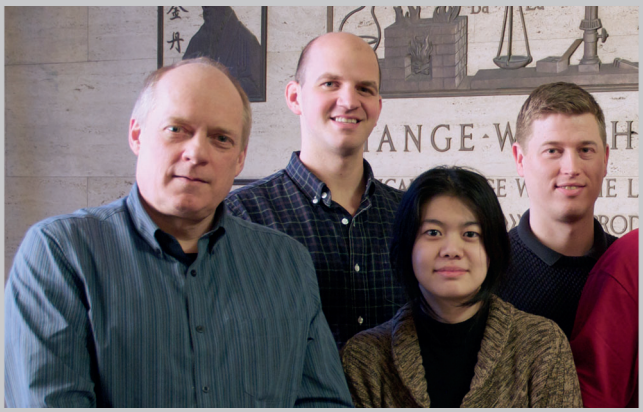


Figure 1. A) A chemiresistor comprising a percolative, randomly oriented network of SWCNTs spanning two metallic electrodes has a current (yellow cloud) flowing through it when a voltage is applied. The presence of an analyte (red sphere) can inhibit current flow (red cloud) through: B) modulation of the Schottky barrier at electrode–SWCNT junctions, C) charge transfer between the analyte and SWCNT, or D) increasing the SWCNT–SWCNT junction distance by intercalation or swelling of the SWCNT network.

Chemistry has provided decades of innovations in molecular recognition to guide the development of chemical sensors. The challenge is how to produce specific electronic perturbations by analyte binding.

In this Review, we survey the area of NW sensors. First, we lay out performance parameters employed to evaluate progress. We then move on to compositions, fabrication methods, device architectures, and operational modalities. Rather than a comprehensive review, we discuss selected examples to highlight the advantages of NW sensors, the status of the field, and opportunities for going forward, which we hope will provide a basis for future innovations.



Authors, from left to right: Prof. Dr. Timothy M. Swager, Dr. Jonathan G. Weis, Sophie Liu, Dr. Jens Ravnsbæk, John F. Fennell, Jr., Dr. Katherine Mirica, Joseph M. Azzarelli, Dr. Sébastian Rochat.

2. Sensory Device Performance Parameters

The performance of a chemical sensor is a product of the physical form of the sensor material, strength of the analyte transduction event, selectivity of the response to a given analyte, and the sensor's stability. Figure 2 shows a representative sensing trace that may assist in graphically visualizing key terms.

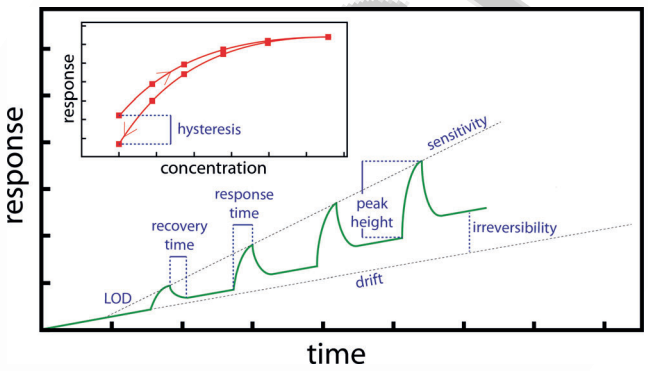


Figure 2. Graphical representation of selected performance parameters in a device successively exposed to increasing concentrations of analyte.

2.1. Sensitivity, Dynamic Range, Limit of Detection

The limit of detection (LOD) is the minimum amount of analyte that can be detected at a known confidence level.[9] The target LODs in sensors for environmental safety are driven by regulation. Representative values are published by the United States Environmental Protection Agency,[10] the National Institute of Occupational Safety and Health (NIOSH),[11] and the European Union Agency for Safety and Health at Work.[12]

The LOD can be influenced by receptor–analyte interactions, surface area, functionalization, and signal amplification. A low LOD is closely tied to high sensitivity (response per unit concentration). The extent to which an analyte influences the electronic properties of NWs is a major factor in the LOD of chemiresistors[13,14] and chemicapacitors.[15]

Chu et al.[16] demonstrated that the alignment of receptors can be used to improve the LOD (Figure 3). A surface-

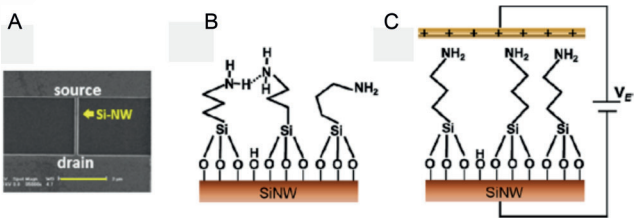


Figure 3. Alignment of aminopropyltriethoxysilane (APTES) on Si NW FETs by an electric field. A) SEM image of a Si NW FET. B,C) Schematic illustrations of the possible APTES molecular structures before and after the alignment process. Reprinted from Ref. [16] with permission. Copyright 2013 American Chemical Society.

modified Si NW field-effect transistor (FET) achieved LODs of 0.1 fM for ssDNA and 0.5 ppm for alcohols. The authors deduced that the field creates structural order to increase the efficiency of molecular reactions, strengthen the molecular dipoles, and consequently improve sensitivity. The reorganizations are likely more complicated than shown in Figure 3B,C, as APTES generally produces multilayer, polymerized coatings.

An increase in surface area offers more sites for analyte–sensor interactions and lowers the LOD. Yue et al.[17] obtained high surface areas in ZnO NW devices by growing them on 3D graphene foam, thereby increasing the surface area from 6 to 33 $m^2 g^{-1}$ and with a LOD of 1 nM for uric acid and dopamine, indicators of Parkinson's disease.

Signal amplification of molecular interactions can reveal otherwise undetectable events. Russell et al.[18] employed a rolling circle amplification (RCA) technique to create DNA strands to template the formation of NWs between two electrodes (Figure 4). This turn-on method detected synthetic and bacterial DNA at 100 pM and 66 fM, respectively.

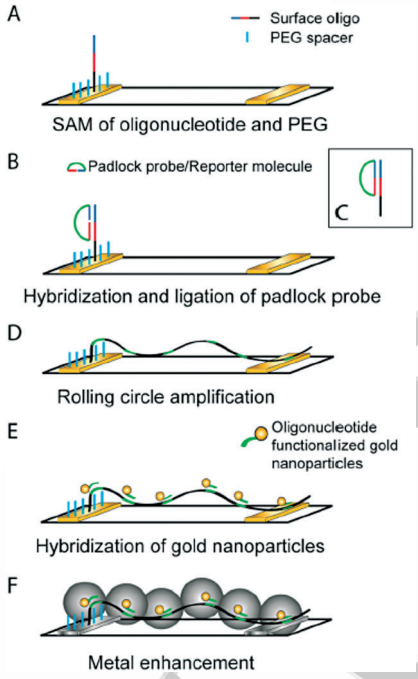


Figure 4. Formation of metalized wires from stretched rolling circle amplification (RCA) products to generate an electrical signal. Reprinted from Ref. [18] with permission. Copyright 2014 American Chemical Society.

Bounded by the LOD and limit of linearity,[9] the dynamic range is the range of analyte concentrations that can be accurately measured by a sensor. NWs can improve the dynamic ranges of sensors by increasing the limit of the linearity (e.g. by increasing the surface area of the sensor to prevent saturation) and by lowering the LOD.

2.2. Selectivity

Selectivity is measured as the ratios of the sensitivity of the target analyte to that of interferents. Specificity should be reserved for cases of ultimate selectivity. Researchers must choose relevant interferents to effectively demonstrate selectivity.

Membrane coatings can exclude interferents based on analyte size, affinity, or permeation time.[19] The operating temperature of a sensor will also affect the selectivity. Increased selectivity can also be achieved by using a separate device to bind and preconcentrate an analyte before thermal desorption onto the sensor.[20–22] Many sensors derive selectivity from functionalization with recognition elements that interact selectively with an analyte. In Section 6, we discuss how functionalization can impart selectivity.

2.3. Stability

Stability is determined by the sensor's ability to produce the same output for an identical input over time, and is quantified as a ratio of the response of the aged device relative to that of a new device. A stable sensor should remain unchanged over the lifespan of the device.

NW functionalization has been explored to improve stability. Our group demonstrated how SWCNTs functionalized with trialkoxysilane moieties exhibit increased robustness (Figure 5). Hydrolytic polymerization affixes the SWCNTs in place on the glass substrate. These sensors can survive sonication in methanol.[23] Alternatively, coatings can be used to stabilize devices by functioning as a barrier to reactive chemicals or by immobilizing NWs.[23–27]

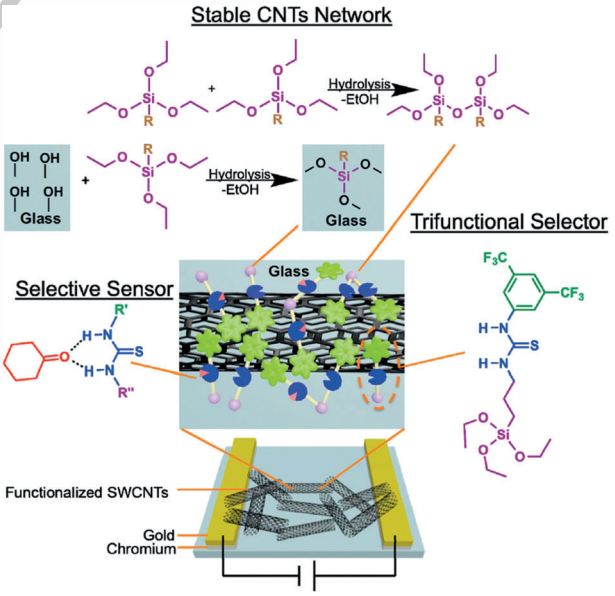


Figure 5. Creation of a highly stable SWCNT sensor by polymerization of a functional selector around the deposited NW network. Reprinted from Ref. [23] with permission. Copyright 2013 American Chemical Society.

2.4. Drift

Drift is the stimuli-independent change of a measurable output over time. It can lead to uncertain results, false alarms, and the need for frequent recalibration or replacement of sensors. Furthermore, there is a dearth of discussion on drift in the literature. There can be both short- and long-term drift, and the difference between the two can in some cases allow one to deconvolute specific contributions.[28–30] Some potential causes include reorientation of particles and domains, segregation of mixtures, sublimation/evaporation of components, adsorption of species, doping/de-doping, and charge migration. The high surface area of NWs creates a challenge for drift, and how to mitigate these factors without passivation needs further exploration.

Drift can be addressed either by in-device recalibration[31] or algorithmically during data processing and/or workup, for example, by using principal component analysis (PCA).[30] However, many applications cannot sustain intensive computational solutions to sensor drift. Therefore, the challenge of drift must be addressed at the device level.

2.5. Hysteresis

Hysteresis is the difference between outputs when an analyte concentration is approached from an increasing and decreasing range.[32] It is important to minimize as a result of the challenges it poses to reversibility and dynamic range. When this suppression is not possible, the best one can do is characterize the hysteresis of the sensor.

2.6. Response Time, Dead Time, Rise Time

Response time is determined at 90% of its final amplitude after analyte exposure,[33] dead time is the time it takes to reach the first 10% of its final signal, and rise time is the difference.[34] The response time is critical, as many applications employ sensors to activate systems in response to changing analyte levels.[32] The factors that govern response time mirror those of reaction kinetics: surface area,[35] temperature,[33] and catalysis.[36]

2.7. Reversibility and Recovery Time

Reversibility is the extent to which the signal is restored to its initial state prior to analyte exposure.[37] The recovery time is the time to decrease to 10% of the peak amplitude after removing the analyte. Although irreversibility can be exploited in dosimetry, incomplete, sluggish recovery is often undesirable.

Remedies to promote complete recovery include heating the sensor[14,38,39] or exposing the sensor to ultraviolet (UV) light.[40] However, heat and UV treatment create more complex systems, with difficulties such as baseline noise and attenuated device lifetimes. Further investigations into alternate solutions for irreversibility are needed.

3. Nanowire Types

We define a NW as a high aspect ratio nanostructure capable of charge transport. Wire does not imply an intrinsic metallic electronic state; most NWs in chemical sensors are in fact semiconductors. Semiconducting polymers, which can be considered as molecular wires, were first recognized as affording signal amplification prior to the extensive efforts on NW sensors.[41–43] However, we will restrict ourselves to a more conventional description of NWs: high aspect ratio materials that are larger than a conventional polymer chain and often polydisperse in terms of length, diameter, and composition.

3.1. Elemental Semiconductor NWs

NWs fabricated from Si and Ge have been extensively studied in sensors, especially in FETs.[44–47] Si NWs are popular as a result of their compatibility with Si electronics and because Si doping and functionalization are mature technologies. However, they have limited stability and oxidize quickly, thereby resulting in surface passivation. Silica NWs (SiO_2 NWs), however, have been substantially documented as an excellent material for sensing applications because of their ease of modification, functionalization, and biocompatibility.[48]

Si/Ge NWs can be synthesized through methods such as thermal evaporation.[49,50] A common technique for growing various inorganic NWs is the vapor-liquid-solid (VLS) method by using chemical vapor deposition (CVD) processes.[51,52] Laser ablation can be used with the VLS method.[53] Si/Ge NWs can also be grown from solution using a supercritical fluid-liquid-solid growth method.[54]

3.2. Metal Chalcogenide or Pnictide NWs

NWs of chalcogenides such as SnO_2, ZnO, TiO_2, In_2O_3, WO_3, V_2O_5, CuO, Cr_2O_3, Nb_2O_5, and Fe_2O_3 and pnictides such as GaN or AlGaN have been used extensively in chemiresistive gas sensors[36,55–57] and FETs.[47,58] Their sensor function often relies on redox reactions between the analyte and the surface, thereby generating variations in carrier concentrations, or surface trapping. They are inexpensive, robust to temperature and resistant to caustic environments, easily integrated into electronic circuits, and give high sensitivity.[59] However, their use in sensing is often hampered by poor selectivity and high operating temperatures.[55,59,60] Nitrogen oxides (NO_x) have been analytes of choice to assess the performance of devices based on metal oxides.[61–64] NWs of oxides can be synthesized by methods[52] that are variations on the VLS method in CVD[44,57,58,65] or catalyst-free thermal oxidation.[57,66,67]

3.3. Carbon Nanotubes (CNTs)

CNTs are excellent sensor candidates due to their mechanical and electrical properties.[68–70] Since Iijima[71] significantly raised the profile of CNTs in 1991, there has been a widespread effort to exploit their properties. CNTs can be considered as long hollow tubes of rolled-up graphene sheets. The angles at which they are rolled (the chiral vector) and the tube diameter determine whether a CNT is semiconducting or metallic. CNTs are either single-walled (SWCNT) or multi-walled (MWCNT). MWCNTs consist of multiple concentric layers of SWCNTs. In defect-free tubes, the bonds between carbon atoms in the sidewalls are sp^2 hybridized, and noncovalent van der Waals forces or π stacking dominate the intermolecular interactions. CNTs are synthesized by laser ablation,[72] arc discharge,[71] CVD, and combustion.[73–75] CVD is the premier method, with mild conditions, high yield, simplicity, and facile mediation of physical characteristics.[76,77] Recent reviews can be found on CNTs in biotechnology and drug delivery,[69,78–80] electronics,[81] energy production and storage,[82–84] and catalysis.[85,86]

CNTs have found a special place in the sensor community because of the aforementioned properties, compatibility with organic chemistry for functionalization,[87] and easy integration into electronic circuits.[88] CNTs have been used to sense biological molecules[89–95] and vapors of industrial gases and explosives.[23,96–102]

3.4. Transition-Metal NWs

Metal-based NWs such as Ni, Pt, Pd, Au, Ag, Pb, and Co have found limited applications in chemical sensing compared to their semiconducting counterparts,[55] but Group 10 NWs excel in H_2 sensing,[47,55,103] Ag NWs for NH_3 sensing,[104] Au NWs for alkanethiol sensing,[105] Ni and Cu NWs for carbohydrate sensing,[106] and organothiol-functionalized Au NWs for biosensing.[53] Metal NWs can be synthesized by chemical etching[105] or reductive cation electrodeposition.[103,107] Metal NWs can be synthesized by bulk solution-phase methods, where a polyol is used as both the solvent and reducing agent for metal cations.

3.5. Conducting Polymer NWs

Conducting (or conjugated) polymers (CPs) are a class of materials that are semiconducting upon oxidation or reduction (doping).[108] Their molecular construction allows for intimate integration of receptor units into the backbone. Sensing relies on inducing modification into the band structure or structure, which results in changes in the electronic properties.[108] Many reviews exist on these materials as sensors.[109–112] We restrict this discussion to NW constructions created from CPs.

Polymers in 1D structures are formed by oxidative polymerization and can have improved electrochemical capacities.[113,114] Templated synthesis relies on physical supports (hard template) to create nanostructures or on molecular self-assembly to guide the growth of CP-based NWs (soft template). Template-free syntheses also exist.[115] Electrospinning of nanofibers allows control over the size, alignment, morphology, and surface functionalization.[116,117] Nanolithography methods allow reproduction of a pattern on a surface.[118,119] CP NW films can also be deposited by layer-by-layer (LbL) methods, Langmuir–Blodgett (LB) techniques, inkjet printing, dip-coating and spin-coating, drop-casting, electrophoretic deposition, and thermal evaporation.[120,121]

Sensors based on FETs (organic field-effect transistors, OFETs, and organic electrochemical transistors, OECTs) and chemiresistor architectures have revolutionized sensing by using CPs with short response times, high sensitivity, easy device integration,[108,120] and room-temperature operation.[120] The CPs can serve as a receptor layer, transducer, protective coating, or electronic circuit.[122] Sensing with nonfunctionalized CPs is mostly limited to small molecules (e.g. HCl, NH_3, hydrazine, chloroform, acetone, acetonitrile, alcohols, and benzene)[123,124] and cations (e.g. Cu^{2+},[125,126] Ag^+,[127] Pb^{2+} and Cd^{2+},[128] and K^+ and Ca^{2+})[129] in solution and reactive gases (e.g. H_2, N_2H_4, NH_3, H_2S, HCl).[122] CPs can be functionalized and included in formulations to improve sensor properties.[130] Long-term instability, irreversibility, and poor selectivity are the main drawbacks of CPs in sensing.[120]

4. NW Assembly and Sensor Fabrication

NW devices can be classified by the number of NWs (one or many) and orientation (aligned, unaligned). Single NW devices have a NW bridging the gap between two electrodes (Figure 6A,B) and offer high sensitivity, fast response to changing analyte concentrations, and high spatial resolution.[131] However, single NW devices require specialized equipment to fabricate, and the low yield of functional devices increases the cost. The Leiber research group has used single-crystalline NWs[132] and n- and p-doped Si and Ge nanowires[133,134] in FETs[135] for the detection of DNA,[136] single viruses,[137] cancer markers,[138] and interactions between small molecules and proteins.[139] The Nuckolls

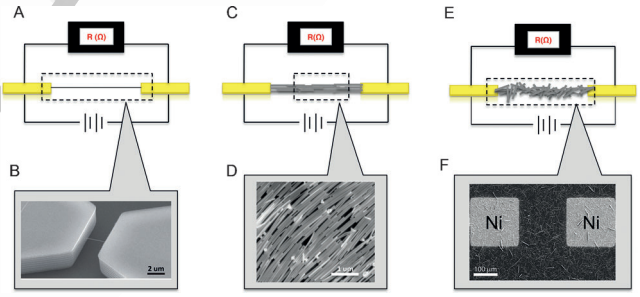


Figure 6. Types of NW devices (schematic representations and images): A,B) Device with a single nanowire; C,D) device with horizontally aligned NWs; E,F) device with a NW network. Figure 6B from Ref. [143] with the permission from 2006 Nature Publishing Group; Figure 6D printed from Ref. [144] with permission from the American Chemical Society 2003; Figure 6F printed from Ref. [145] with permission from the Royal Society of Chemistry 2014.

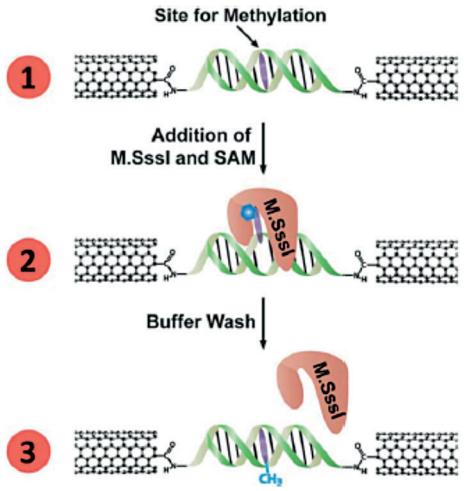


Figure 7. Electrical detection of methyl transferase (M.SssI) binding at a DNA-bridged CNT device. Reprinted from Ref. [142] with permission. Copyright 2012 Royal Society of Chemistry.

research group (Figure 7) has shown novel NW junctions,[140] where SWCNTs are cut and then reconnected by small molecules with probes to observe binding events such as the methylation of DNA.[141] They also bridged SWCNT–SWCNT junctions with DNA, thus illustrating the ability of DNA–nanowire devices to serve as sensors for biochemical events.[142]

Aligned multi-NW devices (Figure 6C,D) have multiple NWs arranged in a single orientation. Compared to NW networks, aligned NW devices have longer mean-free paths for conducting electrons and meet percolation thresholds for connectivity with fewer NW–NW contacts. Accordingly, aligned NW devices can have lower resistance and greater current density, but require complicated assembly processes.

Devices based on NW networks (Figure 6E,F) are those in which the orientation of the NWs is random. The sheer number of NWs results in statistics mitigating the effects of electronic heterogeneity arising from polydispersity in NW length, diameter, and structure. Network devices diminish the need for precise position or orientation of any individual NW, which lowers the difficulty in fabricating devices. On the other hand, network devices have shorter mean-free paths for electrons, thereby leading to higher resistance and lower current density. Networks contain resistive NW–NW junctions that offer prospects for innovative integration of molecular switches.

5. Platform Architectures for Sensor Devices

The electronic properties of NWs are sensitive to changes in their chemical environment. These changes can be electrically evaluated using simple device architectures. A resistor (chemiresistor) is the simplest device with two electrodes (source and drain) on an insulating support connected by NWs (Figure 8A). The resistance can be measured by monitoring changes in the current with a fixed voltage bias across the electrodes.

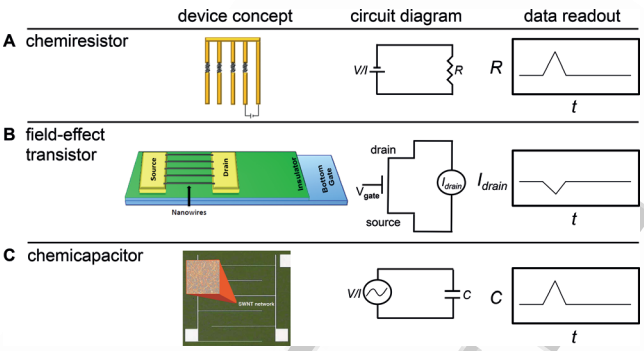


Figure 8. Graphical representation of A) chemiresistor, B) FET, and C) chemicapacitor[15] devices and corresponding circuit diagrams and data readouts.

It can be advantageous to control the carrier concentration when transduction results from charge-transfer interactions between a semiconducting NW and an analyte. An additional electrode (gate) underneath the support converts a resistor into a FET and introduces additional control of the carrier densities through modulation of the applied gate voltage and provides insight into the sensory mechanism (Figure 8B).

Changes in capacitance can also be analyte-specific. The high surface area and prospects for polarizing interfaces are well-suited to creating large capacitive signals (Figure 8C). The use of an AC field for measurements in chemicapacitors can reduce $1/f$ noise, ensure rapid response, and avoid electrophoretic effects from an applied directional voltage, which can reduce drift and enhance reversibility. Moreover, simultaneously examining changes in conductance and capacitance can help increase the specificity.

The analog nature of chemiresponsive circuit components allows for facile integration into wireless devices such as resonant circuits and radio-frequency identification (RFID) antennas. Resonant circuits are comprised of inductive, resistive, and capacitive elements, so chemiresponsive elements directly influence their resonant frequency and Q factor. Our group made use of these features and developed SWCNT sensors that are wirelessly powered and read by smartphones[146] (Figure 9). This method uses the smart-

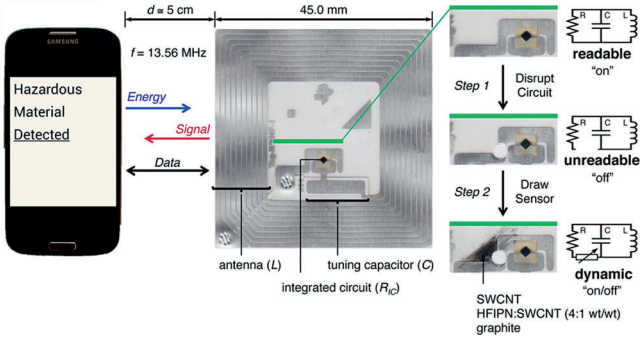


Figure 9. Illustration of a smartphone wirelessly powering and communicating with a passive RFID tag. Reprinted from Ref. [146] with permission. Copyright 2014 Proceedings of the National Academies of Science.

phone's near-field communication (NFC) by cutting the circuit of a passive sensor tag and reconnecting it with chemiresponsive SWCNTs.

6. Functionalization Methods for Applications

NWs display useful intrinsic sensor properties, but functionalization is generally necessary to improve the processability, sensitivity, selectivity, operating conditions, and stability.

6.1. Functionalization of Inorganic Semiconductor NWs

6.1.1. Noncovalent Functionalization of Inorganic Semiconductor NWs

A typical method for functionalizing NWs involves sputtering metal films (Pt or Pd, typically 100 Å) on top of GaN,[147] InN,[148] or Si.[149] In the presence of a Pt or Pd catalyst on the NWs, H_2 binds and dissociates, thereby modifying the carrier concentrations as evidenced by FET measurements.[150] Coating NWs with metals allows for faster, enhanced response and shortened recovery time. Au nanoparticles (AuNPs) were deposited onto GaN NWs by plasma-enhanced chemical vapor deposition (PECVD), and physisorption of gases such as N_2 and CH_4 reduced the conductivity of the NW network.[151] CO_2 sensing was achieved by coating GaN NW transistors with poly(ethyleneimine) (PEI). In the presence of CO_2 and humidity, carbamic acid groups form and ionize to create new charges that affect the transport of the NWs.[152]

Specific detection of biological species is achieved by the functionalization of NWs with receptors possessing high selectivity (enzymes or antibodies).[153] Glucose oxidase was immobilized in a ZnO NW matrix on top of a GaN transistor. In the presence of glucose, the enzyme catalyzes the formation of gluconic acid and peroxide, which translates into a change in the charge on the NWs, thereby allowing for real-time glucose monitoring with a LOD of 0.5 nM.[154] Approaches have also been reported for the detection of biomarkers such as prostate-specific antigen (PSA) by using In_2O_3 NWs functionalized with antibodies through phosphonic acid binding.[155] DNA sensing was achieved at a 10 pM detection limit by electrostatically adsorbing complementary ssDNA onto Si NWs functionalized with amine side chains.[156]

6.1.2. Covalent Functionalization of Inorganic Semiconductor NWs

If an oxide layer is present, silane reactions allow the modification of Si NWs with functional groups (amines, aldehydes) for further functionalization.[138] However, the passivating oxide layer lowers the sensitivity,[157] so the SiO_2 is often etched away, and the exposed surface is covalently functionalized by hydrosilylation, halogenation, alkylation, thiolation, or arylation.[158]

One of the earliest reports on Si-based FET sensing described pH monitoring by APTES-functionalized NWs,[133] and the same type of NWs were found to respond to trinitrotoluene (TNT) in sub-fM amounts in solution and sub-ppt concentrations in air through formation of Meisenheimer complexes.[45] Si NWs modified with thiol groups showed a response to Cd^{2+} and Hg^{2+}.[159] Peptides were attached to Si NWs and used in an array to detect Cu^{2+} and Pb^{2+} in low nM concentrations,[160] and Na^+ was detected by Si NWs functionalized with crown ethers.[46] Volatile organic compounds (VOCs) and small molecules (NH_3, acetone, NMe_3, acetic acid) were detected orthogonally by oligopeptides appended to Si NWs.[161] Many biosensors were developed by appending receptors to Si NWs,[162,163] such as biotin for streptavidin recognition,[164] antigens for recognition of their respective antibody,[137,165] and DNA strands for the recognition of complementary oligonucleotides.[166]

6.2. Functionalization of Metal Oxide NWs

6.2.1. Compositional Mixtures with Metal Oxide NWs

Metal oxides possess many desired properties, but rarely does one exhibit all the desired attributes.[167] Work function and carrier density can be modulated by preparing mixed-metal oxides. Considerable effort has been made to functionalize SnO_2.[58] Gaseous analytes such as H_2S,[168] EtOH,[169–172] CO,[173] H_2,[174] and formaldehyde[175–177] have been detected using mixed metal oxides. Integrating SnO_2 nanocrystals with CuO NWs allows the detection of NH_3 at room temperature.[178] The presence of highly environment sensitive nanosized p-n junctions was given as an explanation for the sensitivity. Copper oxide NWs have garnered attention for the non-enzymatic determination of biologically important molecules. CuO NWs have been used as the active sensing component to determine glucose concentration in concert with a Nafion film[179] and in a Cu-CuO NW composition.[180] In both cases, the NWs electrocatalyze the oxidation of glucose; both devices display high sensitivity and linearity in the biological range of blood glucose (3–50 mM) and environmental stability. Electrochemically synthesized Cu_2O NWs have been employed with Nafion to determine the concentration of H_2O_2 over a wide and relevant range (0.25 μM to 5.0 mM) with a low LOD (0.12 μM).[181]

AuNP-decorated SnO_2 NWs provide enhanced sensing performance for NO_2[182] and aromatic gases ■vapors?■ (i.e. benzene, toluene).[183] Similarly, SnO_2 NWs decorated with AgNPs displayed improved sensitivity and selectivity for ethanol over other gaseous analytes,[184] and PtNP-decorated SnO_2 nanofibers detected acetone in sub-ppm concentrations.[185] More complex functionalization schemes exist where the (doped or mixed) metal oxide is decorated with other nanostructures. A recent example reported Mg-doped In_2O_3 NWs functionalized with metal NPs (Au, Ag, or Pt). Used in an array at room temperature, the sensors were able to discriminate vapors of CO, ethanol, and H_2 at 100 ppm, with the LOD for CO being 0.5 ppm.[186]

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Pagina: 9
Seite: 8te von 18
Umfang (Seiten): 18
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6.2.2. Covalent Functionalization of Metal Oxide NWs

Covalent functionalization has been investigated mostly for biofunctionalization. ZnO can be modified with carboxylic acid or amine functions for further functionalization.[148] APTES was used to functionalize ZnO NWs with uricase to develop a FET sensor for uric acid in aqueous solution.[187] GaN NWs are also amenable to organosilane chemistry, thereby allowing covalent functionalization to afford sensors with high stability.[188]

6.3. Functionalization of Carbon Nanotubes

CNTs offer some of the best opportunities for precise molecular assembly; however, they have considerable imprecision in structure and are mixtures with different diameters, chiralities, and lengths. They also have aperiodic functional groups (defects) that influence their properties. There is still much to learn on how to best functionalize SWCNTs to create optimal NW sensors.

6.3.1. Physical Mixtures Containing CNTs

Functionalization can be achieved by mixing CNTs with selectors, which often leads to composites of lower stability than by covalent modification. The fabrication of metal–CNT composites is achieved through sputtering[189,190] or electrodeposition.[191] Physical mixtures of MWCNTs and PMMA have also been used for sensing CH_2Cl_2 and $CHCl_3$, where the response was ascribed to a swelling mechanism.[192] Solution mixing was used to fabricate SWCNT mixtures with a copper(I) scorpionate unit for the detection of ethylene.[193] In this case, the copper(I) was modeled as binding to the CNT (Figure 10). Finally, physical mixtures of small-molecule selectors and either MWCNTs or SWCNTs have been produced by solid-state mechanical mixing for chemiresistors.[98] This rapid prototyping method allows the screening of CNT composites as sensor materials.[98]

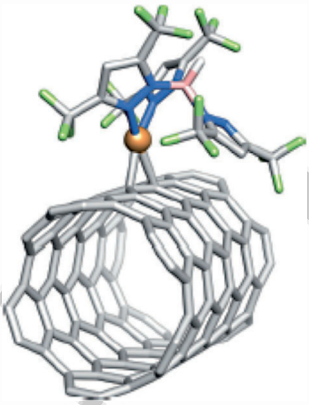

Figure 10. Optimized structure of copper(I) scorpionate bound to 6,5-SWCNT. Reprinted from Ref. [193].

6.3.2. Noncovalent Functionalization of CNTs

Noncovalent modification is less invasive than covalent functionalization as it relies on π interactions and van der Waals interactions between molecules and CNTs. Noncovalent interactions are often integral to CNT dispersions achieved through solution-based mixing, in situ polymerization, or melt mixing.[194] Wei et al. showed the detection of trinitrotoluene (TNT) by using aminopyrene as a selector.[195] Frazier and Swager used a trifunctional molecule containing an aromatic unit (hexafluoroxylene), a selector unit (a thiourea), and an anchoring unit (a silane; Figure 5)[23] to noncovalently functionalize CNTs with superior durability and good sensitivity for the detection of cyclohexanone.

A common strategy is to use polymers. The active materials are typically obtained by drop-casting,[27,196] dip-coating,[197] solution mixing,[198] or in situ polymerization.[199–201] CPs are excellent for dispersing SWCNTs.[202] Polythiophenes with receptor-based side chains have been used in sensors to discriminate between different xylenes (Figure 11).[203]

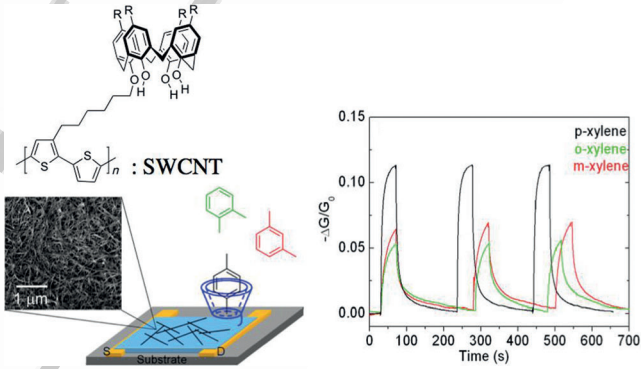

Figure 11. Schematic view of the SWCNT/polymer sensor that selectively adsorbs *p*-xylene. Reprinted from Ref. [203].

6.3.3. Covalent Functionalization of CNTs

Covalent modification disturbs the π-electron system and adds defects, but can increase the stability of dispersions. Common side-wall reactions include dipolar cycloadditions with an azomethine ylide and reductive reactions with diazonium ions.[194,204–206] Covalent functionalization can also be conducted at CNT termini. A common strategy relies on oxidation to produce carboxylic acid moieties at defect sites, which can be further functionalized. Weizmann et al. demonstrated the exclusive regioselective functionalization of SWCNT termini for the detection of single-stranded DNA (ssDNA) using a chemiresistor with detection limits of 10 fM and discrimination of single, double, and triple base-pair mismatches (Figure 12).[207] Oxidation at the end of the tube followed by polymer modification has also been used to build FET sensors with detection limits at the ppb level for NH_3 and NO_2.[208]

Vlandas et al. used the addition of phenyl radicals to demonstrate the covalent functionalization of SWCNT side

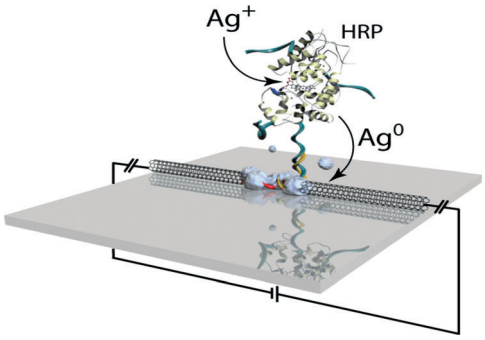

Figure 12. DNA-CNT NWs hybridized with an HRP probe for visualization of a DNA junction. Reprinted from Ref. [207] with permission. Copyright 2011 American Chemical Society.

walls with boronic acids for the detection of glucose at 5–30 mM.[209] Huang et al. utilized a similar approach to functionalize double-walled CNTs (DWCNTs) with aromatic carboxylic acids as a selective sensor for NH_3.[210] The DWCNTs allowed higher degrees of functionalization compared to SWCNTs. Our group has demonstrated the covalent functionalization of SWCNTs by thermal aziridination to introduce amino groups that were further functionalized with hydrogen-bond donors for the detection of cyclohexanone and nitromethane.[96] The covalent functionalization of MWCNTs by using a modular zwitterionic functionalization strategy allowed the formation of diverse densely functionalized materials. Arrays of these materials were used for the detection of a number of volatile organic compounds.[211]

6.4. Functionalization of CP NWs

As discussed earlier, CPs are not, by our definition, intrinsically NWs. However, they can be used to create NWs by templated synthesis or assembled in composite structures with nanofibers or CNTs.

6.4.1. Physical Mixtures of CP NWs

Composites with CPs can produce materials with superior properties, such as high selectivity and sensitivity, enhanced resistance to humidity, low detection limits, low sensing temperatures, and enhanced stability.[212] The rational design of materials that combine CPs with nonconductive polymers,[213,214] carbon-based materials,[215–218] metal nanoparticles[219,220] and oxides,[221] or biological materials[222,223] has been reported. CPs can serve as a matrix for a secondary material or can be decorated with nanostructures in an organized manner.[130,224,225]

Polyaniline (PANI) has been widely investigated and combined with carbon-based materials[226] such as CNTs[215,216] or metal oxides.[221] "One-pot" procedures are used where aniline is oxidatively polymerized in the presence of CNTs.[218] For example, PANI-SWCNT composites are sensors for NH_3 and HCl.[218] Compared to chemically modified polymers, blending materials together avoids complex syntheses, and composite materials may have improved morphology, partition coefficients toward analytes, swelling behavior, as well as mechanical or conductive properties. An additive can also help maintain the properties of the polymer and increase the lifetime.[120] Polymers enable the production of electrospun high surface area nanofibers for gas sensors with enhanced sensitivity and reversibility over bulk films.[227]

6.4.2. Noncovalent Functionalization of CP NWs

Noncovalent functionalization can be accomplished by the deposition of NPs onto the surface of CP fibers. For example, AgNP-decorated PEDOT NWs were found to detect NH_3 with a detection limit (1 ppm) that was fivefold lower than that of pristine PEDOT NWs,[228] and AuNP-decorated PANI NWs show an excellent response to H_2S.[229]

6.4.3. Covalent Functionalization of CP NWs

Covalent modifications have been used to improve solubility, processability, and sensing. These modifications include side-chain, copolymer, and graft functionalization.[120] Many schemes have been developed to immobilize biocompatible receptors onto polymers to enhance the stability under aqueous conditions.[230] Polypyrrole (PPy) is particularly amenable to covalent functionalization because the nitrogen atom can be functionalized. NWs functionalized with PPy-NTA (nitrilotriacetic acid) chelators were found to detect Cu^{2+} cations at sub-ppt concentrations, and the Cu^{2+} complex could be used to detect His-tagged proteins.[231] Polypyrrole (CPPy) NWs functionalized with carboxylic acid groups were found to improve the immobilization onto APTES-functionalized surfaces through covalent linking, with the remaining carboxylic acid moieties available for bioconjugation. FET sensors based on this scheme were developed for proteins.[232] The nitrogen position of PPy was functionalized with biomolecules, and the materials were used to detect cancer antigens (CA125),[233] bacteriophages,[234] bacterial spores,[235] or human serum albumin.[236]

7. Future Developments

The last two decades have produced many innovations in nanofabrication, and we are in an opportunity-rich environment for the creation of functional NW sensors. The sensor designer must continue expanding the range of options to tackle problems of selectivity, drift, sensitivity, and stability. Improved understanding of the basis of analyte detection in NW sensors is needed to guide this development. We suggest areas of need and opportunities for the inspired sensor researcher.

7.1. Improving Selectivity

To many critics, a fundamental limitation is that chemical/biological sensors often lack the ability to identify an analyte unambiguously.[237] It is true that high-resolution mass spectrometry can give near-perfect identification of small, readily

volatilized molecules. Even so, front-end separation by gas or liquid chromatography is often necessary. There has been massive investment in creating portable spectrometers, but these systems generally sacrifice precision for portability and only offer incremental advances. In most cases, NW sensors will not provide superior identification. However, they provide useful information at a fraction of the cost by eliminating the need for expensive electronics, power supplies, and physical structures.

Broad adoption of NW chemical/biological sensors will require improvements in selectivity. Solutions will involve a combination of innovations in the integration of molecular recognition as well as in increasing computational innovations and the dimensionality of sensing data.

7.2. Mitigating Sensor Drift

The effects of drift can be mitigated through data manipulation[29,30] such as baseline correction or reference device normalization but remains a fundamental limitation that hinders adoption in applications, especially for continuous monitoring and for ultralow-cost devices without the power or computational budget to execute these techniques.

The key to minimizing thermally induced drift is developing new techniques that limit nanoscopic rearrangements of sensor components in thin films. Covalent methods, such as cross-linking, that bind NWs to themselves or the substrate should continue to be developed, and matrices may also decrease the drift and improve device lifetimes.

When the NW transducer and selector are distinct, drift can be minimized by strengthening the binding of the selector to the NW to mitigate phase segregation. Tethering can be accomplished by covalent attachment[96,211] or by increasing the number or strength of noncovalent binding moieties.[238]

Drift is also induced electrically and is dependent upon the strength of the applied field. This contribution to drift can be minimized by decreasing the voltage bias, performing a medium-to-high voltage AC pretreatment to accelerate equilibration processes, or using thermal or UV treatments to release trapped charges. Devices that operate under instantaneous applied voltage instead of a static electric field should drift less per unit time; passive radiofrequency (RF) devices are a promising platform. Less drift should lead to longer device lifetimes. It may also be possible to mitigate drift by creating dynamic fluid environments that maintain equilibrium. Indeed, mucus protects the mammalian olfactory epithelium,[239] and designer fluids could selectively partition and transport analytes to sensors.

7.3. Improving Sensitivity

Strategies for enhanced sensitivity include the following: 1) The design of molecular recognition elements where analyte interactions are intimately coupled to carrier transport/generation/depletion. Innovations here can be made by bottom-up chemical designs by employing molecular recognition, designer NWs with engineered work functions, coupling of biological recognition/catalysis, and nanostructures. 2) Developing sensors that leverage junctions between NWs and electrodes. Schottky barriers[36,103,149] and swelling-induced expansion of tunneling barriers[113,122,216,240] have been introduced as important mechanisms. A major opportunity lies in placing responsive materials/molecules in the tunnel junction that can be chemically triggered to have resonant electronic states with the NWs. Rectifying interfaces between p- and n-NWs can also provide opportunities for amplification in analogy to gain produced by avalanche photodiodes. 3) Complex signals can be used to minimize noise, and combinations of resistive and capacitive responses need to be understood. Advances in capacitive sensing are possible by utilizing charge polarization along the length of NWs isolated by resistive junctions. Space–charge contributions to a material's dielectric constant are much larger than simple dipolar effects. Effectively harnessing space–charge changes in chemical/biological sensors will involve careful positioning (orienting) of NWs, controlling the electrical transport and dielectric coupling between NWs, and choice of optimal fields and frequencies.

7.4. Mechanistic Analysis of Responses

Ideal designs exploiting the aforementioned mechanisms require comprehensive understanding of their contributions to NW sensor responses, which remains elusive. Deconvolution of sensor-response contributors is a challenge that holds great promise for the field. In addition to informing rational design of molecular recognition and their implementation in NW sensors, the ability to extract multidimensional information out of a single NW sensor device is an attractive prospect. NW FETs and resonant circuits[241] hold promise as device architectures capable of accomplishing this task, but advances in multidimensional experimental design will be required.

7.5. Current and Emerging Applications

The first consideration when designing a NW sensor should be its environment. Common environmental problems include temperature, humidity, interferents, EM effects, and biofouling. One must also consider how data will be retrieved and how often, which leads us to consider power requirements and sensor stability. If the sensor operates for a long period and operates passively, then a coin-cell battery and a predetermined data logging time interval may be optimal. Conversely, if data are required on demand, a larger on-board power source may be required. Novel approaches to powering sensors include triboelectric methods,[242–245] remote photo- or thermal power harvesting, and resonant inductive coupling. The concept of coupling NWs into devices capable of wireless power transfer is relatively new, but early reports are promising.[242,246–250] One must also consider whether the sensor will be in a durable or expendable form■ok?■.

Next, one must consider how the analytes are likely to encounter the sensing element. Point surveillance is often sufficient for object-level monitoring, while area surveillance

may be necessary for situational awareness in a large 3D space. Area surveillance requires more than one sensor and, therefore, the total cost of goods should be considered.

Selectively recognizing an analyte is perhaps the heart of sensor design. Analytes are categorized as VOCs, oxidizers and reducers, particulates, biological macromolecules, and viruses and bacteria. The ability to detect VOCs continues to improve as molecular design principles are introduced and coupled to NWs. Oxidizers and reducers are often detected by exploiting their influence on carrier concentrations and the Schottky barrier. Greater efforts are needed to detect particulates because of their vast size, shape, and charge dispersity. Biological macromolecules can be targeted by leveraging nature's biomolecular machinery, but this is not a general design approach. Viruses and bacteria interact by multivalent processes, and translating these collective processes into robust signals that are discernable from other events is needed. Robust inexpensive trace virus and bacterial detection has far-reaching implications for human health and safety.

The fidelity of information is of critical importance in chemical/biological sensing. The vast majority of chemical sensors have low specificity, and practitioners often assume that more data from, for example, a large sensor array is better. However, Occam's razor is generally the best approach, with inspired designs that produce high specificity in individual sensors. Such sensors can serve their purpose without an unnecessarily expensive or cumbersome design.

Reversible sensing is generally specified for most applications. However, for many situations where crossing a threshold is relevant, an irreversible dosimeter can be employed that conveys information about the history of the device.

New approaches to extracting more information out of a single sensor or device are beginning to emerge.[251] By combining multivariate extraction of orthogonal parameters with statistical techniques such as PCA, discrimination between analytes with an array is possible.

There is a new sensor paradigm on the horizon. The trend is moving from discrete comprehensive data collection to continuous, parsimonious data collection. Such a move will require the deployment of wireless distributed sensor networks that are linked directly to cloud storage. Chemists, material scientists, physicists, and practitioners will need to work together to develop new modalities that minimize cost per sensor and cost per sensed event. Additionally, opportunities will unfold for fusing chemical information with other inputs to derive new insights about our environment and behavior.

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Reviews

Sensors

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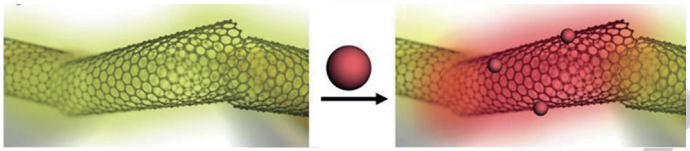
Nanowire Chemical/Biological Sensors: Status and a Roadmap for the Future



Down to the wire: Sensors based on chemiresistance can be readily integrated into electronic devices and are low priced compared to conventional analytical devides. This Review illustrates the advantages of such sensors, which transduce the binding or action of an analyte on a nanowire or nanowire arrangement into a signal. ■ok?■

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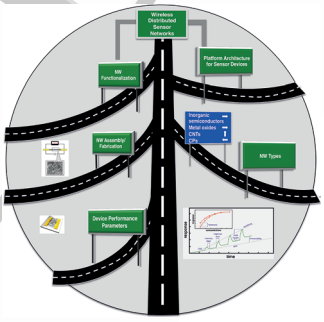

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