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Primer

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Chemiresistive sensing with functionalized carbon nanotubes

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Abstract

Chemical sensing has a vital role in promoting security and welfare. Functionalized carbon nanotubes (CNTs) possess unique electronic, mechanical and chemical properties, rendering them as exceptional transducers for developing highly sensitive, selective and robust chemical sensors. In this Primer, we discuss the progress and challenges associated with chemiresistive sensing using functionalized CNTs, providing an introductory overview, spanning from theoretical to experimental aspects. Various covalent and non-covalent CNT functionalization strategies that contribute to enhancing the sensitivity and selectivity of chemiresistive sensors are discussed, along with their respective merits and drawbacks. Additionally, this Primer focuses on the critical facets of experimental design, including material selection, device architecture and fabrication and best practices for sensor testing. This Primer also discusses the significance of rigorous data interpretation, analysis and reporting, ensuring reproducibility and reliability. Finally, this Primer highlights the existing limitations of CNT-based chemiresistive sensors and investigates potential strategies for enhancing sensor selectivity and sensitivity that may broaden their applicability in diverse fields, from environmental monitoring to biomedical diagnostics. By emphasizing the need to understand the molecular interactions between the sensor and target analyte to improve selectivity, this Primer aims to offer a comprehensive understanding of the current state of CNT-based chemiresistive sensing.

Sections

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Introduction

Chemical sensors have become essential tools for detecting target analytes in various applications, including detecting industrial gas emissions[1], automobile exhaust monitoring for air quality[2], monitoring of greenhouse gases[3], biomolecule detection for disease diagnosis[4,5], methods to ensure agricultural and food safety[6] and the detection of hazardous materials in national defence and security[7]. Meeting the desired requirements of high sensitivity, selectivity, stability, low power consumption, ease of use and long lifetime is crucial for the adoption of chemical sensors in many of these applications[2,5,8]. Conventional analytical techniques such as gas chromatography–mass spectrometry (GC–MS) are widely used and offer high accuracy, specificity and reliability[9,10]. However, disadvantages such as high cost, time-consuming sample preparation and bulky stationary equipment limit the real-time monitoring of applications using conventional analytical techniques[11]. Chemical sensor development has focused on meeting the need for distributed real-time sensing, with the development of sensors based on calorimetric, catalytic, potentiometric, amperometric and chemiresistive transduction[12]. Chemiresistive methods are of increasing interest because of their simplicity in fabrication and sensitivity to realize the continuous monitoring of target analytes[13]. The earliest examples of these sensors operated at high temperature and lacked chemical functional groups[14]. As a result, specificity was a major issue, but advances in recent years have shown a marked progress in the formation of selective chemiresistive sensor platforms[8,15,16]. A chemiresistive sensor displays changes in electrical resistance in response to a chemical interaction, and the sensing materials dictate the performance of the sensor[17,18]. Sensing materials used in chemiresistive gas sensors include metal oxides[15,19], conducting polymers[20], metal–organic frameworks[16], 1D nanomaterials (carbon nanotubes (CNTs)[21], silicon nanowires[22] and metallic nanowires[23,24]) and 2D nanomaterials (graphene[25], transition-metal dichalcogenide[26] and MXenes[27]). Semiconducting metal oxides (SMOs), which possess highly tunable transport properties, have been widely used as sensing elements in chemiresistive gas sensors[3,13,15]. However, the elevated operating temperature required by these sensors results in high power consumption and drift issues, thereby limiting their practicality in distributed sensing networks or wearable devices[8]. Moreover, SMO-based sensors are plagued by low analyte selectivity because of their high operating temperatures[26,28], which prevent the use of molecular recognition methods. Nanomaterials offer an alternative to chemiresistive sensors with lower operating temperature and versatile form factor, owing to their high reactivity and processability[18,29]. CNTs, which possess exceptional physical and electronic properties, tunable selectivity, mechanical strength and miniaturization potential, have emerged as promising candidates for sensing materials in the development of highly sensitive and selective chemiresistive sensors for distributed real-time sensing[21].

CNTs were first discovered in 1991 (ref. 30) and have since been extensively researched for their potential applications[31,32]. These 1D carbon materials possess a hollow cylindrical shape, resembling a rolled-up graphene sheet, in which the direction of rolling is described as the chirality of the CNT (Fig. 1). Single-walled carbon nanotubes (SWCNTs) can be represented by rolling up a single graphene layer, whereas rolling up multiple graphene sheets produces multiwalled carbon nanotubes (MWCNTs). CNTs have the same atomistic structural basis as graphene and are built up from carbon atoms with sp^2 hybridized sigma bonds and a delocalized π-electronic system to create hexagonal rings in a honeycomb lattice[33]. CNTs display an exceptionally large aspect ratio in which their diameters are typically under 10 nm, whereas their length can reach micrometres. The strong carbon lattice endows CNTs with exceptional mechanical strength, with Young's modulus higher than 1,000 GPa (refs. 34,35). The synthesis of CNTs can be achieved through various methods including chemical vapour deposition (CVD), plasma torch, laser ablation or arc discharge[36–39]. The electronic properties of SWCNTs are determined by the chiral vector. The structural configuration of SWCNTs (zigzag, armchair or chiral type)[40] is described by the chiral (roll-up) vector with indices n and m. Specifically, the relationship between n and m dictates whether SWCNTs display metallic or semiconducting properties[31]. For example, zigzag ($m = 0$) and chiral ($n \neq m$) SWCNTs are semiconducting, whereas armchair SWCNTs with $n = m$ and chiral SWCNTs when $n - m$ is a multiple of 3 are metallic, displaying charge mobility above 1,000 $cm^2\ V^{-1}\ s^{-1}$ (refs. 41,42). MWCNTs generally have at least one shell of their base SWCNTs that is metallic and hence are often considered metallic. The unique combination of electrical and mechanical properties of CNTs makes them attractive for applications in nanoelectronics and as transducer materials in chemical sensors[21,31,43–45]. Owing to the chemiresistive sensitivity of CNTs at room temperature, heating elements are not generally required during sensor operation or after analyte exposure[21].

Understanding the sensing mechanisms is crucial for the development and optimization of CNT-based chemical sensors. The chemiresistive response of a sensing material to analytes is governed by its properties and the nature of its interaction with the target analyte. Deducing the specific mechanisms underlying the response of CNT-based sensors continues to be a subject of interest[46–48]. The electronic properties of CNTs are characterized by the band structures of the extremely delocalized π systems[49]. Therefore, predicting or understanding CNT-based sensing mechanisms using chemical intuition alone is challenging. The general sensing mechanisms of CNT-based chemiresistive sensors can be categorized into intra-CNT interactions, inter-CNT interactions and Schottky barrier modulations[21] (Box 1 and Fig. 2).

This Primer provides a concise introduction to the fundamental concepts of CNT-based chemiresistive sensing, including the underlying mechanisms, experimental techniques and result analysis. Furthermore, the typical applications of CNT-based chemiresistive sensing across various fields are outlined. Guidelines for sensor reporting and evaluation, as well as strategies for enhancing sensor selectivity and sensitivity, are outlined. The limitations and future challenges are also discussed.

Experimentation

To perform chemiresistive sensing with functionalized CNTs, the typical workflow includes functionalizing the CNTs, fabricating sensing devices, setting up the testing system and conducting chemiresistive measurements. This section outlines the common approaches to achieve these objectives.

Functionalization of CNTs

The graphene sidewalls of SWCNTs provide high sensitivity to their chemical surroundings. However, they do not display sufficiently specific interactions with analytes, so functionalization is required to make selective sensors[21]. Before the assembly of a chemiresistive sensing device, CNTs are often functionalized to provide sensitivity and selectivity towards specific targets. The functionality can have different degrees of selectivity and modes of action. For example, functionality can provide broad selectivity for classes of compounds, these

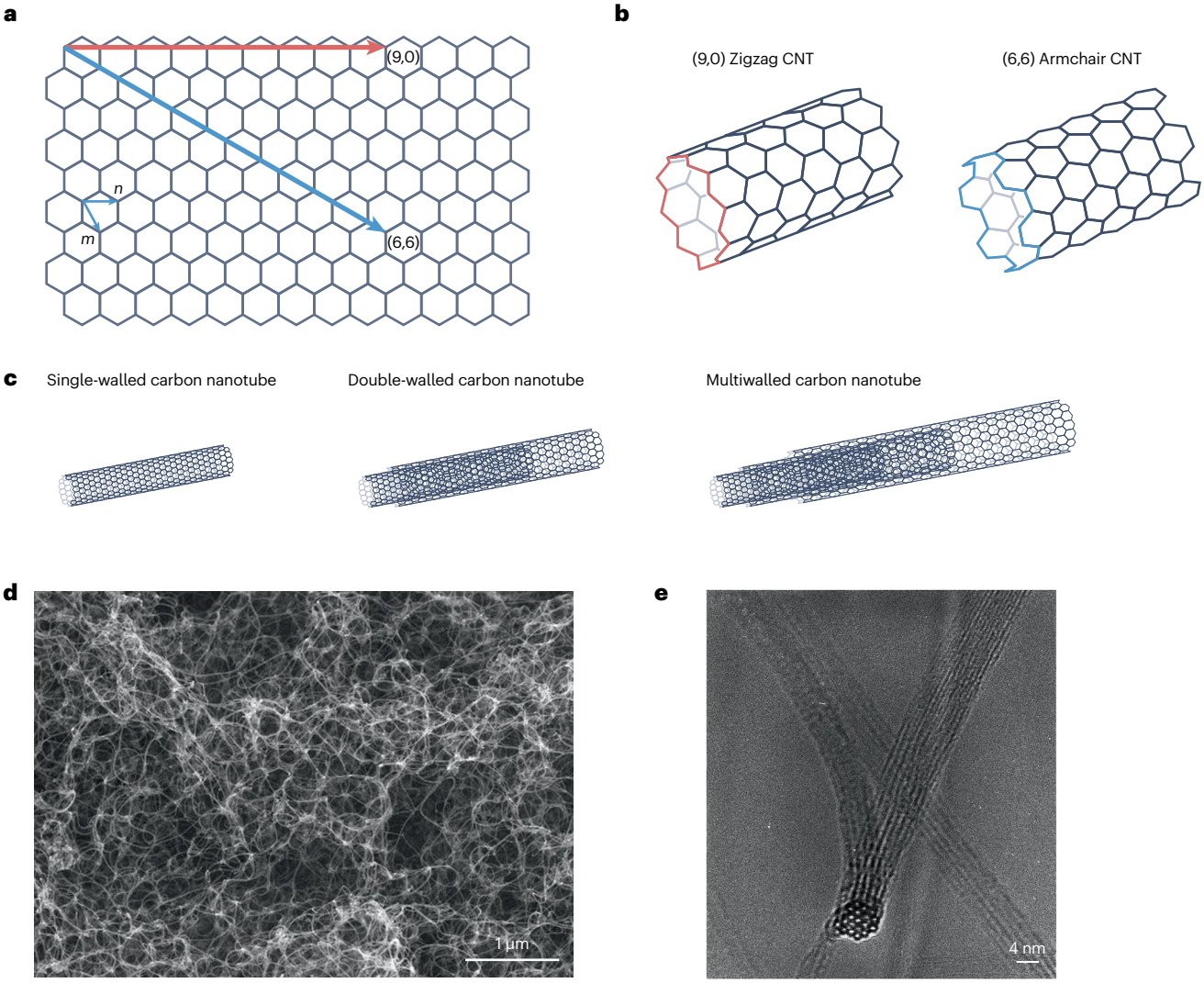

Fig. 1 | Structural configurations of carbon nanotubes. Schematic drawing of carbon nanotube (CNT) chiral vector (part **a**), zigzag and armchair single-walled CNTs (part **b**), single-walled, double-walled and multiwalled CNTs (part **c**). Scanning electron microscopy (part **d**) and transmission electron microscopy (part **e**) images of SWCNT bundles. Parts **a**–**c** reprinted with permission from ref. 31. Copyright 2011 American Chemical society. Parts **d** and **e** reprinted from ref. 36, Springer Nature Limited.

functional groups are generally referred to as selectors. A receptor can also be added with a defined structure for a particular analyte. This attribute is known as a lock and key relationship[50]. Synthetic receptors are often geometrically constrained with macrocyclic or 3D structures, but natural systems can include DNA sequences or receptor proteins[51]. The functional groups can also be catalysts that, through a reaction with an analyte, can affect CNT carriers or create secondary signals that then interact with the CNTs[52]. In their pristine form, CNTs comprise only carbon atoms and some physisorbed oxygen, and additional reactive handles need to be introduced to achieve sensitive and selective detection of analytes. Moreover, the strong π–π interactions among CNTs make them difficult to disperse in common organic solvents and they will quickly form aggregates (bundles) after being un-bundled with intense sonication[53]. Functionalization can improve the solubility and processability of CNTs by preventing rebundling. Furthermore, functionalized CNTs can be integrated with other types of sensing materials such as SMOs, 1D or 2D semiconductors to form heterojunctions that enhance the sensor sensitivity[54–56]. There has been an extensive effort to develop methodologies for the functionalization of CNTs that are broadly classified as covalent and non-covalent modifications[45,53,57–60] (Box 2 and Fig. 3).

The nature of the CNT is connected to the performance and the role of functionalization. In the case of MWCNTs, only the outer graphene surface readily interacts with the environment. In this case, the intra-CNT-sensing mechanism is ineffective because blocking electronic transport in the inner tubes is not possible. As a result, MWCNT-based sensors will largely transduce analyte interactions by inter-CNT mechanisms, and aggressive chemical functionalization of the outermost graphene surface of the CNT can generate favourable sensing behaviour[61,62]. By contrast, SWCNTs not only come in different

Box 1

Sensing mechanisms

Intra-CNT interactions

Intra-carbon nanotube (CNT)-sensing mechanisms involve interactions between the analyte and CNTs (individual or bundles) and modify the number and mobility of charge carriers. Analyte interactions can modulate the conductance of CNTs by inducing direct or indirect charge transfer, which alters the concentration of the majority charge carriers. Notably, physisorbed oxygen molecules on the surface exhibiting weak charge transfer interactions cause CNTs to be p-doped under ambient conditions[265]. Upon exposure to n-type (electron donating) dopants, the concentrations of holes (positively charged carriers) decreases, leading to an increase in resistance. By contrast, p-type (electron-accepting) dopants have the opposite effect where the conductance of CNTs increases[43]. Thara-CNT conductance modulation is regarded to be the primary mechanism for chemiresistive sensing of polar analytes[145]. In addition to charge transfer types of interactions, dipolar potentials can cause carrier pinning (or unpinning) and electrostatic barriers, which give rise to intra-CNT resistance changes[21]. The generation of chemical defects on the CNT sidewalls is another example of an intra-CNT-sensing mechanism, wherein a decrease in CNT conductance is observed, owing to a reaction with an analyte that disrupts the π-conjugation of the CNT surface[116,266].

Inter-CNT interactions

The inter-CNT-sensing mechanism originates from the changes in the intertubular electron transfer. The simplest example is when the distance between the sidewalls of CNT changes. The tunnelling probability of electrons between CNTs decreases exponentially with increasing intertubular distance; hence, even a tiny change in the intertube distance will result in a conductance change in the CNT network[267]. This change can result from the analyte partitioning into the CNT network or the swelling or the disassembly of the polymer or the molecules around the CNTs[104,123,132,268]. The materials between the CNTs could have a more active role, and inter-CNT transport could be gated by electron transfer mediators[65]. The latter mechanism may be operative in some cases, but systems designed to use this design principle are not widely known.

Schottky barrier modulations

Schottky barrier modulations refer to the effects on the junction between CNTs and metal electrodes to modulate the measured conductance[269–271]. This effect is often a smaller resistance change but can be the dominant sensing mechanism when the CNT network is highly conductive and the other resistances are low. For example, devices with a small number of CNTs and CNT–CNT junctions increase the role of the Schottky barrier in the sensor response[272,273]. Overall, the strength of each mechanism will depend on factors including the type of analyte interaction, the defect or the functionalization present on the CNTs and the characteristics of the CNT network. Multiple sensing mechanisms could operate simultaneously such that rigorous characterization needs to be performed to determine the dominant mechanism.

diameters and lengths but also can be metallic or semiconductive. In general, the metallic state is harder to quench and in comparison studies it was found that the metallic SWCNTs displayed lower sensitivity to an analyte trigger relative to the semiconducting SWCNTs[43,63]. It was, however, also noted that metallic SWCNTs were less sensitive to environmental changes in humidity when compared with semiconducting SWCNTs that rely on positively charged carriers[63].

Strategies to enhance sensitivity and selectivity

Pristine CNTs have limited selectivity to analytes, underscoring the necessity for using a selector. The pursuit of ideal selectors, characterized by both high sensitivity and exclusive selectivity towards target analytes, remains an ongoing challenge. Several strategies have been adopted for the rational design of selectors for CNT-based chemiresistive sensing. The development of artificial selectors with near-perfect molecular recognition capabilities is chemically difficult, but the near perfection in some natural systems provides inspiration. This has motivated many synthetic efforts to create guest–host systems that can be coupled to transduction schemes to provide chemiresistive responses. For instance, the Fe(II) porphyrin moiety, a fundamental component of haemoglobin, has been shown to selectively bind to carbon monoxide[64]. The incorporation of these elements into CNT-based field-effect transistors (FETs) produces selective carbon monoxide chemiresistive sensors. Additionally, many other organometallic compounds can potentially be used as selectors for detecting various analytes that exhibit the desired interactions[65–69]. Macrocyclic compounds represent another class of compounds that have preorganized structures and display selective analyte recognition. Crown ethers[62], cyclodextrins[70,71] and calixarenes[72,73] have been utilized as selectors in chemiresistors for detecting different analytes in both gas and liquid phases. Furthermore, the incorporation of elaborate biomolecules, including single-stranded DNA (ssDNA)[74,75], aptamers[76,77], antibodies[78,79] and enzymes[80–82] in CNT-based chemiresistors have proven effective for binding biologically relevant analytes, thereby achieving selective biosensing.

Catalytic transformations, particularly those that result in changes in the oxidation state of transition metal catalysts, can be very effective in creating sensitive chemiresistive sensors. Synthetic chemists have expended considerable effort in creating transition-metal-based catalysis with remarkable chemoselectivity in complex environments, and superior sensors can be constructed by capitalizing on similar designed interactions between a target analyte and a catalytic system. CNTs functionalized with designed catalysts can selectively respond to target analytes that mirror the intrinsic chemoselectivity of the catalysts. Strategies leveraging well-understood catalytic processes have been successfully implemented[52,83–86]. Specifically, SWCNT-based chemiresistive sensors have been engineered in palladium or platinum catalytic cycles wherein the change in the oxidation state of the metal can either decrease or increase the concentration of cationic carriers. Moreover, catalytic transformations that use oxygen and/or water[83,87] are attractive as they can provide intrinsic tolerance of air and humidity

in the resulting sensors. Leveraging selective chemical and catalytic reactions serves as a strong foundation for the design of future sensors.

In addition to improving selectivity, substantial efforts have been directed towards enhancing the sensitivity of CNT-based chemiresistive sensors. One notable strategy involves the polymer sorting of SWCNTs, which results in a more sensitive SWCNT-based transducing material for chemiresistive sensing applications[88–90]. Polymer sorting is a process wherein particular nanotubes are selectively solubilized or dispersed by binding with a polymer or surfactant and can be separated from the insoluble bundled SWCNTs[91]. This sorting is most effective at selecting SWNCTs with different chiralities, diameters and semiconducting/metallic characteristics[92]. As the sensitivity of CNT-based chemiresistors correlates with their semiconducting content[43,63,93], increasing the semiconducting content of SWCNTs is an effective approach for boosting sensitivity. Conjugated polymers are often used in these schemes and have proven utility in purifying and sorting SWCNTs on the basis of electronic and steric preferences[88,91,94–98]. Polymer-sorted SWCNTs have demonstrated higher chemiresistive sensitivity when utilized as transducers, owing to the increased semiconducting content and enhanced purity[63,94–96]. The same methods produce polymer/SWCNT dispersions with superior processability, which is also advantageous for the scaled-up fabrication of sensors[96]. The integration of selector functionality into the sorting polymers is attractive in the latter scheme, and in this case the polymer need not be removed from the final sensing device.

Sensor device architecture and fabrication

In electronic devices, CNTs can be incorporated either as individual CNTs spanning two electrodes or as a network of CNTs. Devices with single-CNT architecture claim to detect single molecules and have simplified sensing mechanisms without inter-CNT effects[99–101]. However, their fabrication and characterization are challenging, and their reproducibility is difficult, owing to variations between individual CNTs and their fragility. Although technically interesting, these sensors are not yet applicable to demanding real-world applications, owing to their low yield and lack of reproducibility. Alternatively, devices constructed from CNT random nanowire networks can be simply cast on devices from dispersions and are more cost-effective and display low device-to-device variance[102,103]. The nanowire networks can also make use of the inter-CNT junctions if target analytes, such as small organic compounds, can partition into the interstitial space between CNTs[104].

As resistive components, CNTs are seamlessly integrated into various electronic device architectures. In the context of chemiresistive sensors, these architectures are typically composed of metal electrodes, namely, source and drain, arranged in parallel or interdigitated configurations on a substrate with the sensing functionalized CNTs deposited in the gaps between electrodes (Fig. 4a). These analyte-responsive resistors are referred to as chemiresistors. This approach offers unparalleled flexibility in architecture design, allowing for the selection of substrates, active materials and circuit design to suit specific applications and power requirements. Simple two-electrode architectures provide several benefits, including ease of fabrication, low cost and operational simplicity that make them ideal for distributed sensors. The ultralow operational power requirements of CNT chemiresistors allow them to be incorporated into passively powered radio frequency identification tags for use in wireless sensor networks[105–108] (Fig. 4b). The integration and miniaturization of CNT-based sensors into various devices, including smartphones, medical instruments and wearable devices, provide for an expansive utility.

CNT-based chemiresistors can be incorporated in a FET architecture, which consists of source, drain and gate electrodes. In this case, the chemiresistive characteristics can be modified by the external applied gate voltage[43]. In these solid-state FET devices, the chemiresistors are again positioned between the source and the drain electrodes, with an underlayer dielectric material mediating the charging by an active gate electrode. Figure 4c illustrates a typical design of a back-gated CNT-based FET sensor using an SiO_2/Si layered substrate. For the detection of solution-phase analytes, FET devices can also be designed with a top-gate architecture, in which CNTs are beneath the metal gate electrode and the electrolyte solution containing the analytes[109,110]. The exposure of FET devices to analytes induces changes in their transfer characteristics, which can be attributed to the alteration in the correlation between the gate voltage (V_G) and the source–drain current (I_{SD}). Changes in the I_{SD}–V_G curve upon analyte exposure can be analysed using techniques such as linear discriminate analysis and machine learning to achieve identification and classification of analytes[111,112]. Additionally, the applied gate voltage can enhance the sensitivity of the CNT-based chemiresistor, and charging can lead to increased interaction with analyte[55,64]. However, to achieve effective modulation with applied gate bias, pure semiconducting SWCNTs are desired in FET architecture. Commercial SWCNT samples, even when highly purified, often contain some metallic tubes[63].

CNTs can be incorporated into electronic devices through two primary methods: growing CNT films grown on a substrate or depositing dispersed CNTs. The former involves high-temperature CVD onto substrates containing pre-patterned electrodes and inorganic substrates[37,113,114]. This method results in robust electrode–CNT contacts and can minimize inter-CNT effects by limiting the number of CNTs grown. However, the precise control of the orientations, diameters and chiralities of CNTs in these devices is challenging, and device yields are low[113]. By contrast, the deposition of CNT dispersions is an alternative method for fabricating chemiresistive devices. This can be achieved using various practical and scalable techniques, such as drop casting,

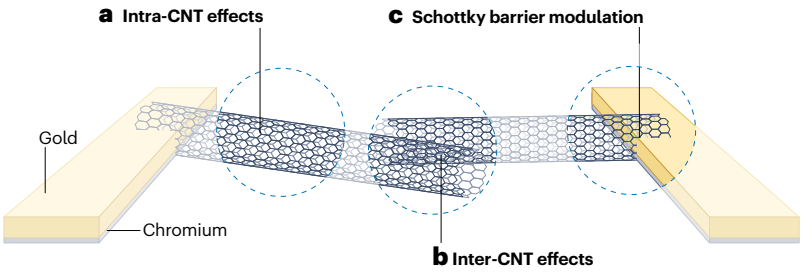

Fig. 2 | Schematic illustration of two single-walled carbon nanotubes bridging two electrodes. The transduct processes can be characterized as changes in the transport or free carrier concentrations in an individual single-walled carbon nanotube (SWCNT) (part **a**), changes in the electron transfer rates between SWCNTs (part **b**) or the result of modulation of the interfaces with metallic electrodes (Schottky barrier) (part **c**). Reprinted with permission from ref. 21. Copyright 2018 American Chemical Society.

Box 2

Covalent versus non-covalent functionalization

Covalent functionalization

Covalent functionalization involves chemical reactions to form new covalent bonds on the graphene sidewalls or carboxylic acid termini of carbon nanotubes (CNTs). These reactions are used to attach groups that can selectively recognize, interact or react with target analytes[61,62,274]. This functionalization can be achieved by oxidation[275,276], halogenation[277,278], hydrogenation[279,280], alkylation[281,282], nucleophilic/electrophilic addition[283–285], radical addition[286–288], cycloaddition[289–292] or post-functionalization modifications of oxidized CNTs[293,294]. Covalent functionalization provides a means to create strong and stable bonds between functional groups and the surface or termini of CNTs for long-term stability with well-defined and precise chemical composition. However, covalent functionalization of the graphene sidewalls can result in rehybridization of the sp^2 CNT carbon atoms to have more sp^3 character, thereby perturbing the intrinsic optical and electronic properties of CNTs[295–297]. Therefore, it is generally essential to control the degree of functionalization to provide sufficient selectivity without too great of a loss of the electronic transport properties. This delicate balance can be achieved by selecting appropriate functional groups and controlling the extent of chemical reactions. Such careful control over the functionalization process can lead to the development of CNT-based sensing devices that are highly sensitive, selective and robust[64,83]. Recent theoretical and experimental studies have shown that by functionalizing CNTs with aziridine or cyclopropyl moieties, the electronic and optical properties of CNTs can be preserved as the electrons around the site of functionalization undergo ring-opening rearrangement to maintain the π surface[227,298,299]. Such functionalization strategies hold the potential to create highly active materials with a high degree of functionalization while maintaining the excellent electronic properties of CNTs.

Non-covalent functionalization

Non-covalent functionalization offers the advantage of minimal perturbation of CNT electronic structure by adsorbing surfactants[300,301], polymers[302–304] and other small molecules[305,306] onto the CNT sidewalls through hydrophobic interactions or π–π stacking. Metal nanoparticles have also been used to decorate CNTs to achieve highly sensitive and selective chemiresistive sensing that mirrors their intrinsic reactivity[307,308]. Polymers and biomolecules, such as single-stranded DNA, have been shown to effectively wrap around CNTs to increase processability and introduce functionality[303,309]. However, these non-disruptive functionalizations often come at the expense of inferior stability, resulting from the intrinsically weak non-covalent interactions. The physisorbed species or the macromolecular coating on CNTs is most often meta-stable and can easily undergo displacement, desorption or phase segregation[21]. These features cause variance in the baseline CNT conductance, sensors ageing unpredictably and even complete loss of functionality. Therefore, the judicious implementation of CNT functionalization is necessary to tailor the chemiresistive device for detecting target analytes within specific contexts.

inkjet printing, spray coating, doctor blading and spin coating[115]. These techniques fix CNTs in place through rapid solvent removal. The solution-based approach is also compatible with CNT functionalization schemes. Substrate surfaces can be treated to react with the deposited functionalized CNTs to strengthen the substrate–CNT adhesion, and these stabilizing features are important for liquid-based sensing applications[116]. Liquid flow can be challenging because it can induce changes in the positioning of CNTs that give rise to baseline conductance drift and general sensor instability. Other techniques, such as alternating current dielectrophoresis and layer-by-layer assembly, can also be used for controlled deposition of CNTs on the substrate[117,118]. Post-deposition treatments such as ultraviolet light irradiation can increase sensor sensitivity, presumably through the selective removal of metallic tubes or addition of defects that interact with analytes[119,120]. Solvent-free methods have also been developed to enable rapid fabrication of CNT-based chemiresistive sensors through the deposition of viscous mixtures (pastes) or nonvolatile mixtures (deep eutectic liquids or ionic liquids) and CNTs on rough substrates[121,122].

Setting up a chemiresistive-sensing experiment

When designing a chemiresistive-sensing experiment, it is crucial to construct a system that can deliver analytes in a robust, controlled and safe manner[44]. A typical schematic diagram of a gas-sensing testing platform is shown in Fig. 5a. The analyte source can be a commercial gas cylinder or vapours of volatile organic compounds (VOCs). Subsequently, the analyte gas is diluted with carrier gas (nitrogen or air) to a desired concentration, mixed and then introduced to a sensing chamber (enclosure) in which the sensors are housed. Inert materials such as stainless steel or polytetrafluoroethylene should be used in tubing, junctions and the sensing chamber to prevent analyte adsorption. The flow rates of the gas streams are controlled individually by mass flow controllers (MFCs), and analyte injection is also controlled by turning on and off the respective MFCs. The flow rates of the diluent gas are typically in the standard litre per minute range, whereas analyte gases are typically in the standard cubic centimetre per minute range to achieve low concentrations. The concentration of the gas analyte in the mixed gas stream can be derived from the vapour pressure and the ratio between the diluent gas and analyte gas. It is recommended to calibrate the analyte gas concentration by additional analysis such as gas chromatography using external standards. Commercial gas generators also produce gas vapours in controlled concentrations from liquid sources. It is essential to maintain a constant total flow rate across the sensing chamber before, during and after the analyte injection to minimize drift in the sensor baseline conductance. Moreover, the humidity level in the sensing chamber can be controlled by introducing an additional gas stream that is bubbled through water at a fixed rate[123,124]. In cases in which toxic or hazardous gas analytes are used, the mixed gas stream at the outlet of the sensing chamber needs to be quenched/processed accordingly to minimize safety/health hazards[86].

For liquid-sensing applications, analyte delivery can be executed in either a stationary solution or under flow conditions (Fig. 5b). In a typical stationary solution experiment, a polydimethylsiloxane (PDMS) mould with punched holes is affixed to the substrate to isolate the liquid-sensing environment and enclose the sensing electrodes[125,126]. The PDMS structure functions as a liquid reservoir, establishing a baseline for the chemiresistive sensor. Analyte addition can be performed through direct pipetting into the PDMS well, creating a solution with the desired analyte concentration. Despite its operational convenience, this approach is limited by slow diffusion kinetics and potential solvent evaporation, which can compromise the consistency of analyte concentration and result in variability in chemiresistive outcomes. Alternatively, analyte delivery can be facilitated in flow using more intricate microfluidic designs, which necessitate greater effort in design and assembly[127,128]. Analogous to gas-sensing configurations, blank and analyte solution flow rates can be effectively regulated by individual pumps to achieve the targeted analyte concentration with efficient mixing. In such systems, the capacity to remove the analyte after the sensing test while maintaining the baseline flow rate enables the assessment of sensor reversibility and recovery behaviour.

Chemiresistance measurements

Essential to all analytical methodologies is the capacity to yield qualitative (for example, binary yes/no outputs) or quantitative measurements. Typically, a small bias voltage/current (for example, 100 mV or μA) is applied across the source and the drain electrodes that connect the CNTs using simple source meters, potentiostats, data logger or even handheld multimeters[83,85]. A time-dependent profile of conductance can be recorded as a function of analyte exposure. Generally, multiple channels can be measured simultaneously to evaluate the device-to-device variance on duplicate devices and to efficiently evaluate multiple sensor compositions. Once the bias voltage/current is applied, a short period of time is required for the system to equilibrate to a steady state with a stable baseline. It is important that the environmental conditions including temperature, total flow rate and humidity are held constant during this period. To mitigate the variability in the environmental conditions during real-world sensing, it is also possible to construct a sensing chamber or a flow cell equipped with pumps and drying elements to better control the flow rate and humidity of the carrier medium for a stable baseline. After a robust baseline has been established, the target analyte can be introduced to the sensing chamber or flow cell. The duration of analyte exposure and sensor recovery can be set, depending on the sensing mechanism and the application scenario to evaluate the sensor performance. In many real-world gas-sensing applications, there is passive transport of vapours to sensors. These environments can be simulated by placing sensors in high-volume (10+ litre) sealed containers and then injected gas with a syringe into the chamber[129,130]. The chamber can be purged to reset. These experiments are not as easy to reproduce, and the kinetics of the sensor response will be highly dependent on uncontrolled convection. As a result, flow cells are most often reported in the literature for testing of sensor performance.

Results

Analysis of sensor performance

Sensor sensitivity. The performance of a chemiresistive sensor is assessed on the basis of its sensitivity, selectivity and stability[21,131]. The evaluation of sensor sensitivity includes the magnitude of sensor response, response time, recovery time, concentration sensitivity and limit of detection. Sensor responses can saturate, meaning that a highly sensitive sensor may be able to give accurate responses at low analyte concentration, but have lower resolution at high analyte concentration. Similarly, less sensitive sensors will not provide accurate measurements at trace analyte concentration. Figure 6a presents a hypothetical chemiresistive sensing trace that characterizes the response of a device to an analyte over time. Chemiresistive sensing data are commonly reported as relative changes in conductance, current or resistance of the device over time[21]. Data processing, statistical analysis and plotting can be readily performed using software such as Matlab or OriginLab.

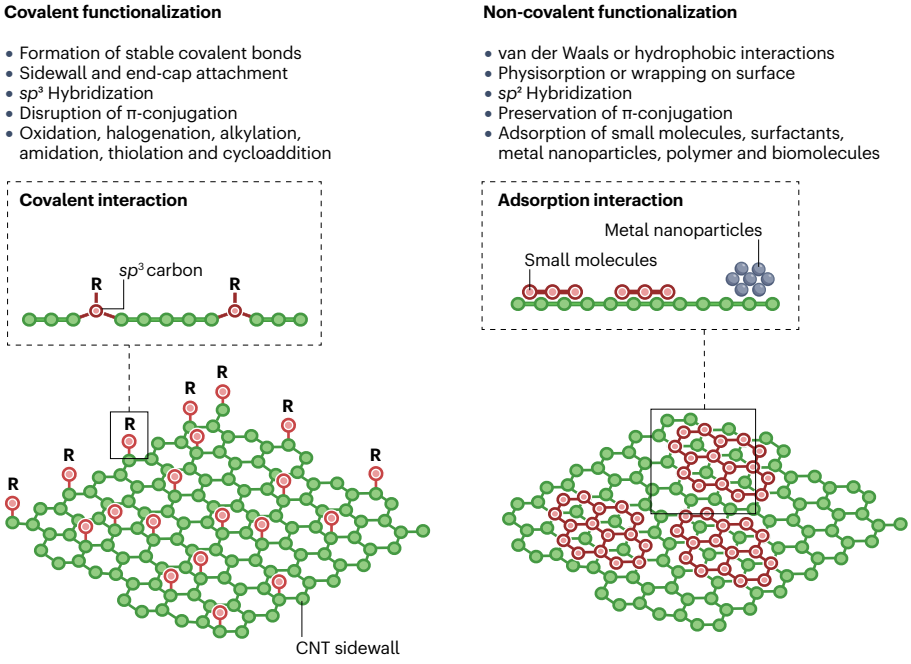

Fig. 3 | Comparison between covalent and non-covalent functionalizations of carbon nanotube. Schematic representation of different types of carbon nanotube (CNT) functionalizations and covalent functionalization (bottom left) and physisorbed selectors (bottom right) on a graphene surface representing the CNT sidewalls. Adapted with permission from refs. 45,264, RSC.

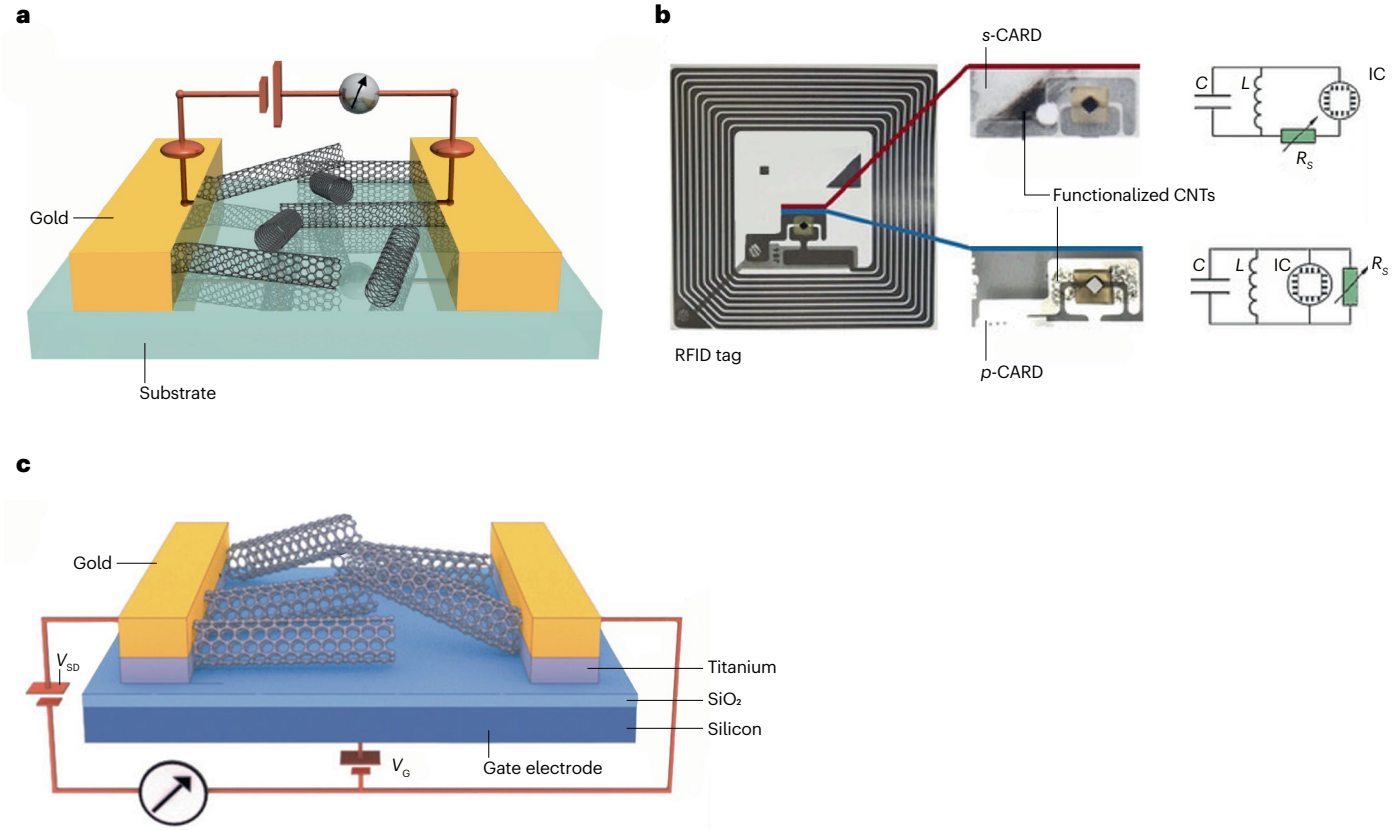

Fig. 4 | Design schemes of carbon nanotube-based chemiresistive devices. **a**, Illustration of a single-walled carbon nanotube (CNT) chemiresistor in which the current is measured between two gold electrodes under the conditions of a fixed applied potential. **b**, Photograph of a passive radio frequency identification (RFID) tag that contains a resonant radio frequency circuit containing a capacitor (*C*), antenna and an integrated circuit (IC). These tags can be converted into chemically actuated resonant device (CARD) sensors by interrupting the circuit and splicing chemiresistive CNTs in series with the IC (*s*-CARD) or in parallel with the IC (*p*-CARD). **c**, A single-walled CNT field-effect transistor sensor schematic shown with a back gate electrode. *L*, inductor; R_S, chemiresistor; V_G, gate voltage; V_{SD}, drain–source voltage. Part **b** adapted with permission from ref. 105, Wiley. Part **c** adapted with permission from ref. 64, Wiley.

Specifically, the sensor response is characterized by the normalized difference in the measured current with a static applied voltage, or the measured resistance changes in response to analyte exposure[21]. To assess the response of chemiresistive sensors systematically and realistically, a standardized protocol needs to be established with an analyte exposure time that is relevant to the real-world deployment of the sensors. Moreover, the response time and recovery time can be derived from the sensing trace. These are critical parameters that quantify the time required by a sensor to generate/recover from a response following exposure to an analyte[15], sometimes referred to as T_{90}. Reversible sensors can return to their initial output following exposure, which is frequently examined in tandem with recovery time. Although it is generally favourable to develop reversible sensors, irreversible sensors can function as dosimeters for the sensitive detection of trace analyte over an extended period[64,132]. Assessing the response time and recovery time informs on kinetics and magnitude of the interaction between the target analytes and the chemiresistors, which can shed light on the underlying sensing mechanism. External factors, such as temperature, gas concentration, flow rate and the design of the sensing cavity (chamber), can influence these results during experimentation.

A chemiresistive sensor is often expected to discern minor variations in the analyte concentration. Figure 6d presents hypothetical sensing traces that characterize the response of a device to increasing analyte concentrations. Plotting the sensor response with respect to the analyte concentrations yields a calibration curve[133] (Fig. 6e). When the response is linear, the slope of the calibration curve corresponds to the concentration sensitivity of the sensor. In some cases, there will be both regions of linear and nonlinear behaviour over the entire concentration range relevant to the application scenarios. The dynamic range encompasses the concentrations used for the entire calibration curve, whereas the linear range denotes the concentration range over which the signal maintains a linear proportionality to the concentration[134]. It is not uncommon for sensors to have multiple linear ranges depending on the range of analyte concentration. Extra care should be taken to determine whether it is appropriate to present the sensor response to analyte concentration in logarithm-based calibration curves, because these plots can underestimate the deviation from linearity and prevent proper evaluation of the sensor sensitivity[135,136]. The lowest amount of analyte that can be detected under specific operating conditions with reasonable certainty is defined as the limit of detection (LOD)[134]. Because of the differences in the conceptual approaches

to LOD, there are several different methods to calculate theoretical LOD[137,138]. A representative and operationally convenient method to calculate theoretical LOD is shown in equation (1), in which the root-mean-square noise (rms_{noise}) of the sensor is determined from the deviation in conductance with respect to time with the appropriate polynomial fit of the baseline[139,140]. The slope is derived from the linear regression fit of the sensor response versus analyte concentration at the lower limits. Although it is generally favourable to develop sensors with low LOD, nonlinearity can limit the applicability of a sensitive sensor to high analyte concentrations as a result of saturation. Therefore, when developing and optimizing chemiresistive sensors, it is crucial to consider the balance between achieving a low LOD and maintaining linearity across the dynamic range to meet application-specific demands.

$$\mathrm{LOD} = 3 \times \frac{\mathrm{rms}_{\mathrm{noise}}}{\mathrm{slope}}, \quad (1)$$

which shows the calculation of theoretical LOD.

Sensor selectivity. Selectivity, interchangeably referred to as specificity, is a crucial characteristic of a sensor, defining its ability to discriminate the target analyte from other interferents within the sensing environment[141]. To assess selectivity, sensors are subjected to common or anticipated interferents pertinent to the environment in which they will operate. The signal differences in the presence and absence of interferents, or the disparity between sensor responses to the target analyte and interferents, determine the selectivity of the sensor. Ideally, a highly selective sensor will recognize the analyte of interest, without interacting with other compounds (Fig. 6f). However, owing to the structural and electronic similarities among individual and classes of analytes, achieving such ideal selectivity is rare in practice. Exceptions are with biomolecular recognition, with DNA being the gold standard[80]. However, even in this case, care must be taken with the temperature and conditions to prevent competitive binding of DNA that is not a perfect complement to the capture strand. Cross-reactivity arises when sensors interact with multiple analytes, often leading to intricate signals and reduced selectivity. Consequently, before asserting the selectivity of a sensor, it is essential to evaluate the sensitivity of the sensor against a comprehensive range of potential interferents, ensuring that the sensor provides accurate and reliable measurements within the context of its intended application. Field testing is key and can reveal if the environment is as anticipated. Additionally, it is crucial to emphasize the significance of oxygen and humidity tolerance in the development of practical and realistic chemiresistive sensors. The presence of oxygen or water molecules can impair sensor performance through competitive binding to active sites or oxidation of the active materials[21,142]. Sensing within air-conditioned buildings provides a very stable low humidity, but exterior sensing at different temperatures is generally challenging. Therefore, it is vital to conduct sensor testing under ambient air conditions and across various humidity levels to ensure reliability in the selected real-world applications.

Sensor stability. Long-term stability is a critical parameter for chemiresistive sensors, as it determines their ability to deliver consistent outputs over time (Fig. 6g). The intended applications should be considered when evaluating the sensor stability. In some cases, for example, with a wearable sensor for monitoring chemical exposures, the sensor may only need to actively function for the shift of one worker, but it may be expected to have a year-long shelf life[29]. In other cases, end users may have expectations of continuous operation for weeks or months. Various factors can undermine sensor stability throughout its operational life cycle including the structural stability of functionalized CNTs, the organization of the CNT network, parasitic electrical effects and irreversible absorption of materials on the sensor[143,144]. The latter has a distinct difference with high-temperature metal oxide-based sensors that operate by decomposing analytes to small molecules and in effect are self-cleaning at the expense of low selectivity[19]. The arrangement of the CNT network can be perturbed by environmental variables such as temperature/humidity changes and light exposure. Long-term stability can be assessed by comparing the sensitivity of sensors of different age and storage conditions that are relevant to the intended applications.

Investigation/determination of sensing mechanism

The chemiresistive sensor field contains many contributions that have at best vague descriptions of why a sensor has specific selectivity. To credibly advance the field of chemiresistors, efforts to deduce or prove the sensing mechanism are imperative. The valuable insights generated will inform future development and optimization to produce more sensitive and selective sensors. The sensing mechanisms of CNT-based chemiresistive sensors are intricate with multiple potential operating

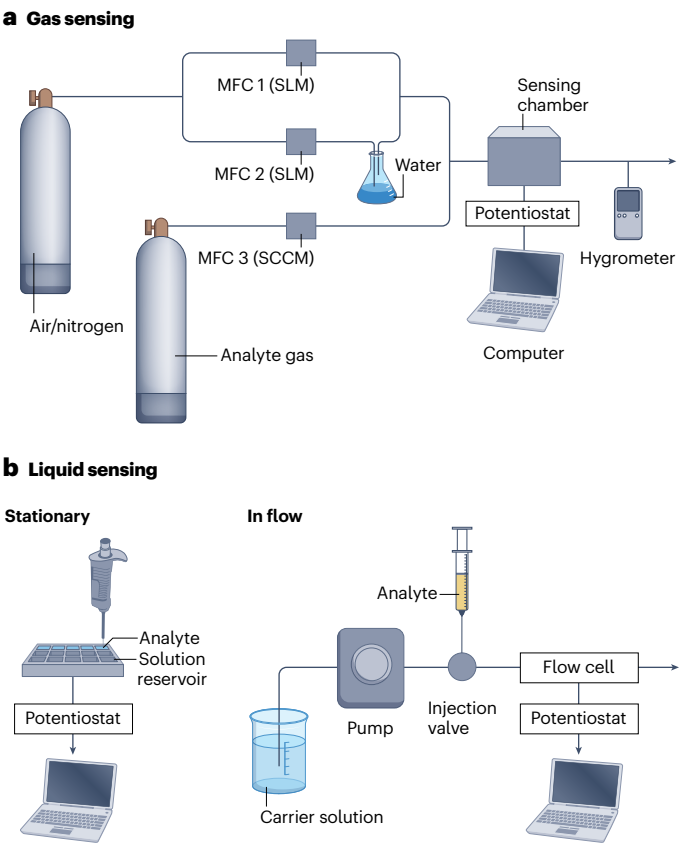

Fig. 5 | Design schemes of chemiresistive-sensing experiments. Typical experimental set-ups for analyte delivery and chemiresistive measurement in sensing experiments with analyte delivery in gas (part **a**) and liquid phase (part **b**). MFC, mass flow controller; SCCM, standard cubic centimetre per minute; SLM, standard litre per minute. Part **a** adapted with permission from ref. 124. Copyright 2019 American Chemical Society.

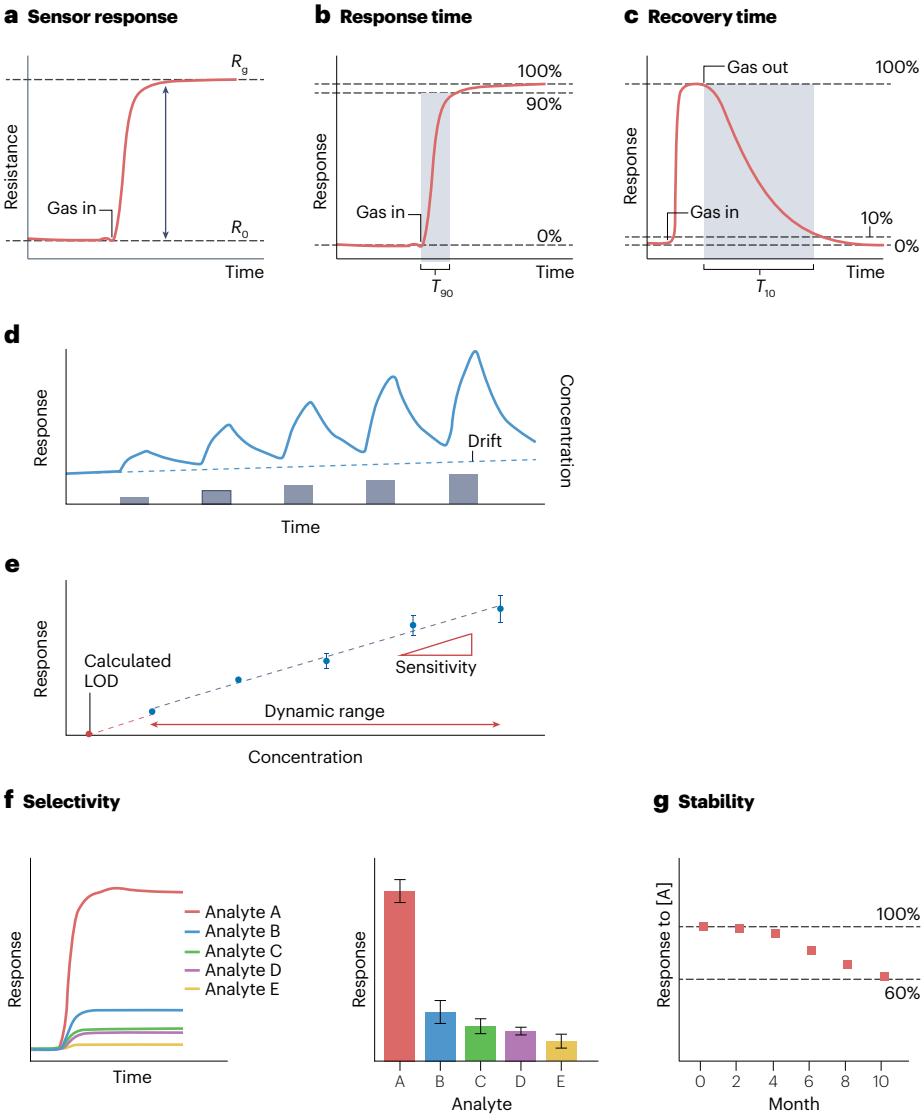

Fig. 6 | Typical characterization of sensor performance. a–**c**, Sensor responses showing the temporal behaviour of the sensors with regard to time, analyte exposure and recovery times in analyte-free carrier gas. **d**,**e**, Sensor drift can often be approximated with a linear baseline correction and the extrapolation of a sensor response plot to give a limit of detection (LOD). **f**, The cross-reactive nature of sensors is illustrated with variable responses to different interferents. **g**, Evaluation of long-term stability of sensors. R_0, baseline resistance; R_g, sensor resistance. Parts **a**–**c**, **f** and **g** reprinted with permission from ref. 15, Elsevier. Parts **d** and **e** reprinted with permission from ref. 131, Wiley.

mechanisms at play. Nevertheless, using chemical intuition and various experimental probes can facilitate the process of distinguishing and identifying the dominant mechanisms involved. For instance, the type of chemiresistive response (p-type/n-type) could provide valuable information on the nature of the analyte–selector interaction[43,145]. A comparison of response of a p-type CNT chemiresistor with an n-type ZnO nanowire with the same recognition element will give opposite responses to an electron releasing analyte-triggered event[83]. A discrepancy between the anticipated analyte-induced change and the observed chemiresistive signals can signify the dominance of an unexpected secondary effect. In chemiresistive sensing in which the adsorbed analyte is anticipated to undergo a chemical transformation, such as oxidation, detecting the reaction product can be crucial for elucidating the sensing mechanism[52,83]. In some cases, this may require model systems that generate larger amounts of reaction products for analysis[85]. For gas-sensing applications, analysing the outlet gas using GC–MS can provide insights into the chemical composition of the gas environment post-sensing[146,147]. Reaction products can also be captured and identified using techniques such as NMR spectroscopy[52,83,148]. Similar approaches can be expected to identify product species in liquid-based sensing applications. In instances in which chemiresistive sensing is expected to cause irreversible changes to the CNT selector, using techniques such as X-ray photoelectron spectroscopy can be beneficial for probing the chemical transformations in the sensing materials attributable to the sensing event[19,149]. The direct monitoring of the sensing elements can also be performed using in situ and operando spectroscopy to evaluate the transient effects during the sensing event that can be indicative of the sensing mechanism[150,151]. Furthermore, the influence of charge transfer on CNT doping levels stemming from their interaction with analytes can be detected through Raman spectroscopy[152,153]. A shift in the characteristic G-band towards higher wavenumbers indicates the presence of an electron-accepting analyte, whereas a shift towards lower wavenumbers suggests an electron-donating analyte[154,155] (Fig. 7a). Raman spectroscopy can also be utilized to assess modifications in surface defects on CNTs before and after exposure to analytes. For example, an oxidizing selector–analyte interaction can cause

disruption of the conjugated sp^2 network in pristine CNTs, resulting in an increase in defect sites on CNTs[116]. This effect can be identified with an increase in D/G peak intensity ratio in the Raman spectrum[156,157]. Changes in the CNT network can also be detected by Raman as the radial breathing modes are sensitive to inter-SWCNT associations[65,72,156].

Assessing current–voltage properties (such as transfer characteristics) using FETs presents a powerful approach for deciphering the sensing mechanisms involved in CNT-based devices[21] (Fig. 7b). Unlike traditional silicon FETs, CNTs can be switched with applied V_G biases to be active as both n-type and p-type majority carriers[158]. FETs with this type of behaviour are referred to as being ambipolar. Various sensing mechanisms can lead to unique changes in the FET transfer characteristics and changes to the potential that the conduction channel is activated for conduction, which is referred to as the threshold V_G (ref. 21). For instance, when electron-donating species adsorb to CNTs, a charge transfer from the analyte to the tube occurs, resulting in an n-type doping effect and shifting the threshold V_G (Dirac point) towards a more negative gate voltage. By contrast, electron-accepting species cause a p-type doping effect, shifting the Dirac point to a more positive V_G (ref. 43). Sensing mechanisms that induce a decrease in charge carrier mobility can also be revealed through FET measurements and can be determined by the I_{SD} (refs. 102,159–161). Furthermore, the Schottky barrier modulation impacts the transport of electrons and holes differently, it manifests an asymmetric change in conductance under different gate bias wherein an ambipolar device current at positive gate voltage might increase with a decrease in current at negative gate voltage[47,162]. Graphene FETs (GFETs) serve as a valuable platform for investigating sensing mechanisms when the same selectors used with CNTs can be transferred to a graphene layer[95]. The GFET-based structure can behave as a model for intra-CNT responses with elimination of the inter-CNT chemiresistive responses. This analysis of transfer characteristics in GFETs can provide a clearer understanding of the selector–analyte charge transfer dynamics.

Applications

CNT-based chemiresistive sensors find applications across diverse fields, and this Primer can only highlight a very small subset of the vast examples in the literature. Interested readers are advised to refer to the recent review articles that offer a comprehensive survey of the topic[1,21,28,44,45,47,131,143,163–168]. These articles provide detailed analysis and discussions of the advancements made in the field of chemical sensing by CNTs.

Environmental monitoring

CNT-based chemiresistive sensors can be inexpensive and distributed, which make them ideal for environmental monitoring in scenarios ranging from greenhouse gas monitoring and leak detection of hazardous gases, to quality analysis of water and soil. Analytes relevant for

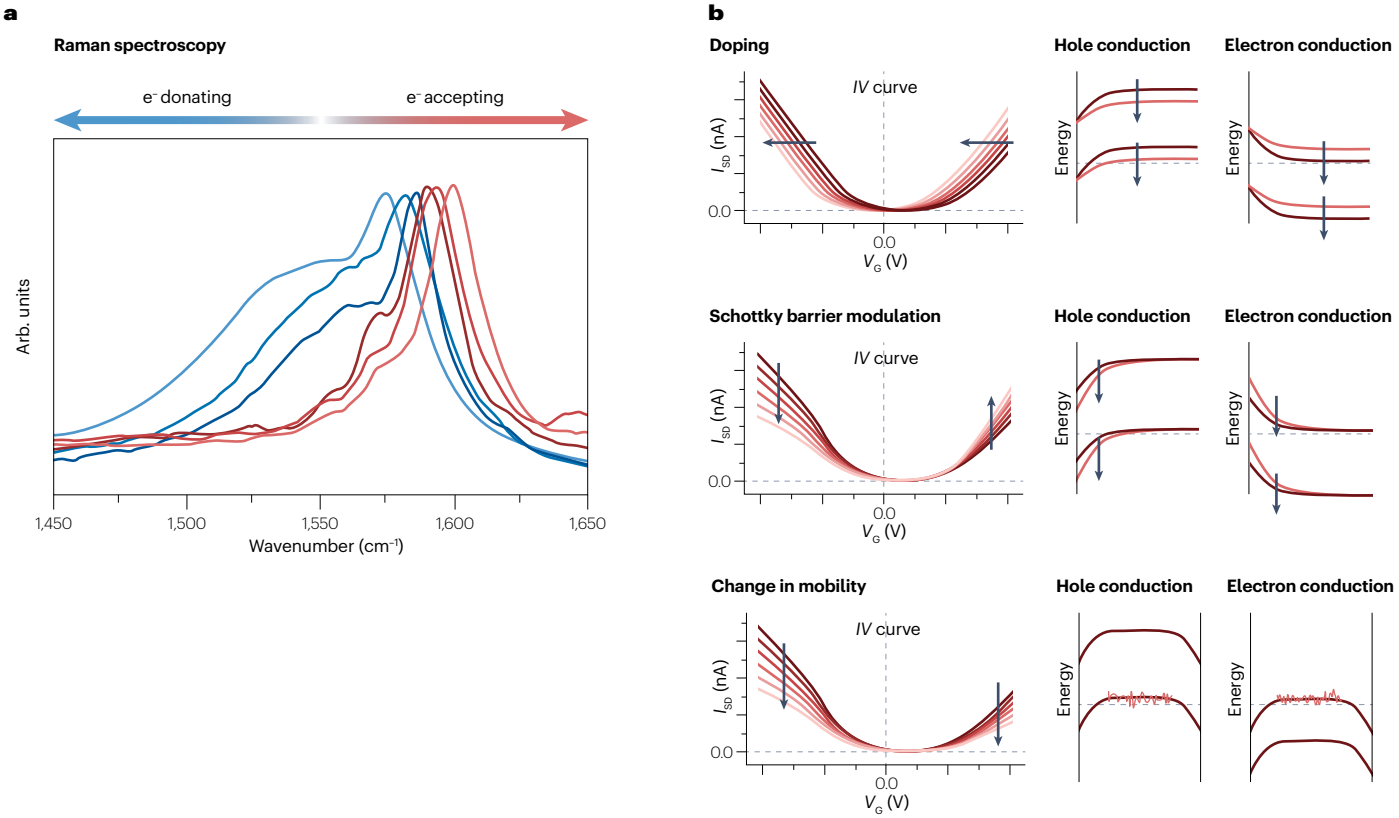

Fig. 7 | Evaluation of sensing mechanism by Raman spectroscopy and transfer characteristics of carbon nanotube-field-effect transistor. a, Hypothetical changes in Raman G-band of single-walled carbon nanotubes when interacting with electron-donating and electron-accepting species. **b**, Hypothetical changes in transfer characteristics and band structure diagrams of carbon nanotube-field-effect transistor in response to analyte exposure in accordance with different sensing mechanisms. I_{SD}, source–drain current; V_G, gate voltage. Part **a** adapted with permission from ref. 154. Copyright 2008 American Chemical Society. Part **b** adapted with permission from ref. 21. Copyright 2018 American Chemical Society.

environmental monitoring include hazardous gases such as ammonia, hydrogen, methane, nitrogen dioxide, carbon monoxide, hydrogen sulfide and sulfur dioxide, as well as VOCs such as aromatic hydrocarbons. In aqueous environments, contaminants of interest include heavy metal ions, organics and perfluoroalkane substances.

Pristine CNTs display reasonable sensitivities to ammonia and nitrogen dioxide[139,140,169–171], which are intrinsically reducing and oxidizing gases, respectively. The introduction of sidewall defects[172,173], metal nanoparticles[160,174,175] and metal oxide nanoparticles[176–178] has been shown to enhance sensitivity. However, these modifications sometimes result in reduced selectivity, owing to nonspecific interactions with interfering species[21]. Polymer–CNT composites have also proven effective in ammonia and nitrogen dioxide detection, wherein a strengthening of the interactions between analytes and specific polymers is proposed to be operative[179–181]. The functionalization of CNTs using metal–organic compounds with extended π systems, such as metalloporphyrins or metallophthalocyanines, represents another effective approach for achieving selective ammonia detection[65,182,183]. CNTs functionalized with gold[184–186], copper[187,188] and tin dioxide[189,190] nanoparticles can impart alternative selectivity and have utility in the selective detection of hydrogen sulfide. Hydrogen sulfide can also be detected using aerobic oxidation (catalysis) mediated by polyoxometalates immobilized on SWCNTs[86]. Selective detection of sulfur dioxide, however, has challenges in selectivity because of the similar electrophilic nature of sulfur dioxide and nitrogen dioxide[169]. Nonetheless, selective discrimination in chemiresistive sensing between these two gases has been accomplished by using their different reactivities as a functional of humidity[191].

There has been particular focus on metal nanoparticles for the detection of hydrogen and methane[142,160,192,193]. Palladium nanoparticles have been extensively used in the functionalization of CNTs, resulting in highly selective and sensitive hydrogen sensors[95,194,195]. By contrast, the development of methane sensors has encountered challenges in achieving selectivity because of the intrinsically more inert nature of methane. Nevertheless, recent advancements in CNT-based chemiresistive methane detection have been reported, using metal nanoparticles[196,197] and molecular platinum catalytic complexes to activate methane molecules[85].

For the detection of carbon monoxide, nitrogen-doped and boron-doped CNTs have been shown computationally to enhance sensitivity to carbon monoxide[198]. Sulfonated and carboxylic acid-functionalized CNTs also respond to carbon monoxide[199,200]. Furthermore, CNTs functionalized with metal nanoparticles and metal oxide nanoparticles have been studied as carbon monoxide sensors[55,160,201,202]. Recently, the non-covalent modification of CNTs with organometallic complexes has shown promise in enhancing the selectivity of CNTs for carbon monoxide detection[64,66,203]. Another effective strategy to enhance sensor sensitivity involves applying gate bias to functionalized SWCNTs on FET devices to increase their interactions with carbon monoxide[55,64].

In a recent study, it was found that FET devices, which incorporate SWCNTs non-covalently modified with iron tetraphenylporphyrin or cobalt tetraphenylporphyrin, display notable sensitivities towards trace concentrations of benzene, toluene and xylenes (BTX)[204]. Alternatively, using a polymer concentrator, such as cellulose acetates functionalized with a 2,3,4,5,6-pentafluorophenylacetyl group on top of SWCNTs, has also been explored[205]. These integrated sensors exhibit enhanced BTX detection capabilities over unmodified SWCNTs, although limitations in selectivity remain. Chemiresistive sensors featuring SWCNTs dispersed by tight-binding pentiptycene-containing conjugated polymers exhibit high selectivity for BTX. This is due to the hydrophobic π-conjugated interstitial cavities formed between the polymer chains and graphene sidewalls, which facilitate preferential adsorption of small aromatic compounds[123]. In the latter case, it was found that cyclohexane displayed lower response and hence a nonspecific swelling mechanism was not operative. Despite the encouraging results of these CNT-based devices in BTX sensing, achieving complete selectivity in BTX compounds using chemiresistive-sensing alone was elusive. Differentiation between BTX or various xylene isomers often necessitates the implementation of sensing arrays[62,72]. Other candidate recognition schemes are SWCNTs wrapped with calix[4]arenes-substituted polythiophene, which displayed selective chemiresistive response that correlates with binding constants with isomers of xylene determined in solution experiments[72].

CNT-based chemiresistors and FET devices have been developed for real-time detection of metal ions. For example, pristine SWCNTs have been used for the dosimetric detection of mercury ions, by promoting the irreversible reduction of mercury ions[206]. In another study, polyazomethine was utilized to non-covalently functionalize SWCNTs for cobalt ion detection. The selectivity is suggested to originate from a conformational change of polyazomethine on complexation with cobalt ion, which modified the network and the interactions between the polymer and CNTs[207]. FET sensors comprising SWCNTs functionalized with an array of polypeptides have also been reported for the selective detection of nickel and copper ions[208].

National security

CNT-based sensors can detect explosives and chemical warfare agents that are respiratory, nerve and vesicant (blistering) agents. These materials represent a substantial hazard to public safety and their prompt detection can help to minimize the impact in the case of event[209,210]. CNT-based sensors provide a promising approach to portable sensing methodologies for national and public security[21].

Although pristine SWCNTs exhibit some sensitivity to nerve agent mimics, such as dimethyl methylphosphonate (DMMP)[211,212], sensors based on CNTs functionalized with polymers such as polypyrrole[213] and substituted polythiophenes[161,214] result in substantially improved chemiresistive responses and selectivity for DMMP. The DMMP selectors investigated include hydrogen-bonding hexafluoroisopropanol[215], *p*-hexafluoroisopropanol aniline[216] and tetrafluorohydroquinone[217]. Moreover, FET devices incorporating CNTs functionalized with ssDNA have demonstrated increased sensitivity to DMMP compared with unmodified sensors[75]. Although DMMP has Lewis basicity and volatility similar to sarin gas, it lacks the intrinsic electrophilic reactivity. Reactivity-based sensing schemes are attractive as they mimic the reactivity of the agent and are expected to react to a family of chemicals that have similar intrinsic toxicity. SWCNTs wrapped with metallosupramolecular polymers have been designed to undergo depolymerization when exposed to diethyl chlorophosphite, which is highly toxic, but can be handled in controlled laboratory environments. It was found that depolymerization of polymer wrappers around SWCNTs creates enhanced SWCNT–SWCNT interactions and produces 1,000-fold increase in conductance[63,106].

A chemiresistive sensor for thionyl chloride, a pulmonary agent simulant, has been reported using SDS-coated CNTs[145]. The proposed sensing mechanism is the transfer of electrons from metallic SWCNTs to thionyl chloride[145]. CNTs have also been functionalized with chlorosulfonated polyethylene and hydroxypropyl cellulose wrappers to

reportedly respond to hydrochloric acid and chlorine selectively[218]. Furthermore, nitrogen-doped CNTs and CNTs bearing nitrogen-containing functional groups have been utilized for chlorine and thionyl chloride detection[219,220]. In addition to organic selectors, inorganic materials such as metal nanoparticles and organometallic complexes have been integrated into CNT-based sensors for the selective detection of chlorine[221,222].

CNTs functionalized with electron-donating carbazolylethylene oligomers have been applied for the selective detection of nitroaromatics in chemiresistive devices[223]. These selectors promote strong interactions with electron-accepting nitroaromatics and enable the successful differentiation among trinitrotoluene, dinitrotoluene and nitrotoluene vapours[223]. The chemiresistive trace detection of nitroaromatics in water has also been achieved using 1-pyrenemethylamine-functionalized CNTs[224]. Alternatively, biosensors using CNTs functionalized with DNA or peptide wrappers have also shown potential in explosives identification[75,225]. Changes in the DNA base sequences was shown to produce selectivity in these schemes[80]. Secondary signatures of explosives, such as solvents used in the production of plastic explosive compounds, serve as an alternative target analyte for the detection of explosives[226]. For instance, the explosive nitroamine (RDX) is recrystallized from cyclohexanone and residual vapours of this solvent have been identified as an important explosive signature. SWCNTs wrapped by polymers with pendant thiourea groups that bind to cyclohexanone produce sensitive chemiresistive cyclohexanone sensors with reproducible robust responses under demanding conditions[227–229].

Agriculture monitoring and food safety

The advantages of CNT-based chemiresistive sensing include compact dimensions, low energy consumption, easy operation and the capacity to identify many different analytes, making them suitable for food and agriculture-related applications. Gas sensing relevant to food management and agricultural production includes the monitoring of fruit ripening, flower maturity, packaging integrity and detection of meat spoilage.

CNT-based sensors can be integrated into smart packaging. Here, an integrated sensor may inform on maturation of fruit, if a modified atmosphere packaging has been compromised allowing oxygen ingress, if food spoilage has progressed or if food had been treated with a pesticide. CNT-based detection of the plant hormone ethylene[230] can be used to monitor fruit[69,231] in retail settings, detect ripening in cold storage[84,232] or determine optimal harvest times. Trace ethylene detection by CNT chemiresistors can be used to monitor the senescence of purple lisianthus and red carnations, which are accompanied by sub-ppm level ethylene concentrations[83]. The real-time monitoring of food spoilage with CNT-based sensors can prevent the consumption of spoiled food products. Volatile biomarkers related to food spoilage that can be detected include hexanal in spoiled milk[233] and biogenic amines in spoiled fish and meat[67,234,235]. Passive radio frequency identification CNT-based oxygen sensors have been integrated into food packaging to evaluate the integrity of the modified (inert) atmosphere that provides for extended shelf life[108]. Furthermore, food quality can also be evaluated for taste and aroma of the food item using CNT-based sensors[236,237].

Health diagnostics and biosensing

The future of health care will include an increasing number of diagnostic tests. To best serve patients and reduce costs, increases in speed of diagnostic tests and frequency of use are desired. Cost reduction and connectivity via the cloud to doctors are also driving interests in point-of-care diagnostics. In this context, CNT-based chemiresistive sensors offer ideal portability and accessibility, particularly for the detection of volatile biomarkers in breath analysis and the detection of important biomolecules such as proteins, whole cells, glucose and DNA[143,163,165].

CNT-based sensor arrays have been engineered to discriminate among various VOCs by utilizing SWCNTs functionalized with diverse selectors[238,239], including metalloporphyrin complexes[65,240], or MWCNTs that are covalently functionalized with a diversity of selector groups[62]. These arrays have demonstrated effectiveness in distinguishing VOC classes without the interference of humidity. Besides CNTs functionalized with metal nanoparticles and metal oxide nanoparticles, selective polymer-wrapped CNT-based sensors have also been developed to detect inorganic gases including ammonia[241], NO_x (refs. 94,96), carbon dioxide[159,242] and hydrogen sulfide[243]. These inorganic gases function as biomarkers to suggest medical conditions such as renal failure[244], halitosis[245], asthma[246] and gastrointestinal disorders[247].

Glucose oxidase has been used as the selector in chemiresistive and FET glucose sensors[163,168]. Direct immobilization of enzymes on CNT electrodes can lead to denaturation and leaching[163]. To overcome this, molecular[82] and polymeric linkers[116,248] have been used to anchor glucose oxidase onto CNTs, resulting in good stability and chemiresistive responses. Non-enzymatic CNT-based glucose sensors have also been developed, showing low limits of detection and linear ranges without interference from background species in bodily fluids and blood serum[249,250]. Chemiresistive approaches to glucose sensors have demonstrated excellent sensitivity, prolonged stability and real-time monitoring of glucose concentrations.

Many CNT-based DNA sensors are based on immobilizing ssDNA and monitoring conductance change that is modulated directly or indirectly by hybridization with the complementary DNA[163]. Examples have shown successful identification of mutant alleles[251] and DNA base pair mismatches[74]. It is worth highlighting that CNT-based FET devices are also capable of quick and accurate detection of proteins and cells in biological media[77,164,166]. Label-free biosensors using CNTs have gained popularity for their simplicity, high sensitivity and rapid detection[77,251]. Leveraging antibody and aptamers recognition elements to promote specific biomolecule adsorption to the CNT surface was found to create effective FET biosensory responses.

Reproducibility and data deposition

Meticulous documentation of CNT functionalization, sensor fabrication and sensing experiments is paramount for ensuring reproducibility in CNT-based sensor research. This process encompasses outlining methodologies for each stage, enabling researchers to comprehend, replicate and potentially enhance the used techniques. CNT functionalization is crucial for introducing desired sensor sensitivity and selectivity and demands detailed reporting of functionalization methods, associated chemicals, reaction conditions and purification steps. These factors influence the resulting CNT-based sensor performance[63,64,83,124]. Sensor fabrication considerably affects the performance, stability and sensitivity of a sensor[170,171]. Thorough descriptions of fabrication methods, such as substrate choice, surface pretreatments, deposition or integration techniques (for example, drop-casting, inkjet printing or CVD), device assembly and encapsulation or protective measures, are required. Delineating the experimental set-up for sensing tests is vital, including analyte concentrations, exposure durations and environmental factors such as temperature, humidity, carrier gas type and

Glossary

Arc discharge
A method for synthesizing carbon nanotubes through arc-vaporization of two adjacent graphite electrodes in an inert gas.

Chiral (roll-up) vector
A lattice vector in the hexagonal graphene sheet that defines the structure of a carbon nanotube by specifying the direction and distance of the rolling/wrapping of the graphene sheet.

Device hysteresis
The phenomenon in which the output of a device depends not only on its current input but also on its past inputs, resulting in a lag or variance in response.

Dosimeters
Sensors that provide an integrated measure of exposure over a time period and are ideal for applications such as monitoring cumulative exposure of an individual to toxic chemicals.

Intra-CNT interactions
Sensing mechanisms involve interactions between the analyte and individual carbon nanotubes (CNTs) or CNT bundles, which modify the number and mobility of charge carriers.

Inter-CNT interactions
Sensing mechanisms originate from the changes in the intertubular electron transfer.

Pristine CNTs
Carbon nanotubes (CNTs) in their original, unmodified state, without any functionalization or doping, often used as a baseline for comparison in sensor performance studies.

Recovery time
The time required to accomplish a 90% recovery on removal of the target analyte under the background gas or liquid.

Response time
The time needed for the sensor to achieve 90% of its maximum response.

Schottky barrier modulations
The effects on the junction between carbon nanotubes and metal electrodes to modulate the measured conductance.

Selectors
A component of a sensor system that provides specificity, enabling the sensor to distinguish between different analytes in a complex mixture.

flow rates. Reporting electrical measurement parameters (for example, applied voltage and current) and data acquisition or analysis methods is also essential. These sensing results and experimental metadata can be deposited to an online data repository to facilitate big data analysis and learning[252]. To ensure the reliability of analyte concentrations used in sensing experiments, using certified calibrated sources or performing analyte calibration with external standards via techniques including NMR or GC is recommended.

Assessing consistency and stability of a CNT-based sensor involves conducting repeated measurements over time with multiple analyte exposure cycles for reversible sensors. To rigorously evaluate the sensor consistency and stability, comprehensive statistical analysis (linear discriminant analysis, analysis of variance and principal component analysis) should be performed[253,254]. Allowing the sensor to recover between successive analyte exposures establishes the baseline with its associated drift and facilitates the evaluation of device hysteresis[131]. Mitigating hysteresis effects can enhance the reliability and accuracy of a sensing device. Moreover, examining sensor sensitivity across electrode configurations and sampling schemes contributes to determining consistency and reproducibility. A base process entails subjecting different sensors, fabricated using identical methods, to the same test conditions and comparing responses. Inconsistencies in sensor performance may indicate issues with fabrication, functionalization, electrode–CNT interfaces or sensing mechanisms, necessitating further investigation. Finally, investigating the selectivity of a sensor requires verifying that the sensor maintains selectivity after exposure to interferents, which could potentially affect the sensitivity of a sensor irreversibly. Ensuring that there is no detrimental effect by interferents gives confidence in the selectivity and overall performance of a sensor. Promising sensors that are expected to leave the laboratory for field testing should be tested under simulated conditions, such as passive diffusion of the analyte and over the expected temperature and humidity ranges[21].

Limitations and optimizations

CNT-based chemiresistive sensors are far from ideal and have several limitations. Contrary to the controlled laboratory testing conditions in which the background environment and analyte injections are well controlled at recorded times, field deployed systems will often experience environmental and chemical variances that are sporadic and irregular in magnitude and duration. This necessitates accurate deconvolution of signals from the baseline for the successful identification of the sensing signals. Long-term stability poses a challenge for CNT-based sensors, drifts in baseline conductance can be induced by humidity, temperature or flow rate changes[21]. Alternative sensing techniques wherein external stimuli initiate sensing events, such as thermal, optical or acoustic sensor triggers, can potentially produce enhanced reliability and minimize the impact of the long-term sensor drift. It is always of interest to evaluate sensors in regulated sensing chambers with carefully managed environmental parameters to decrease the baseline drift. An alternative approach to potentially address the challenges of baseline drift in CNT-based chemiresistive sensors is to utilize photoexcitation as a component of the chemiresistive sensing[185,255]. By using this external stimulus to activate or modulate the output of the sensor, sensors can provide enhanced sensitivity and selectivity with more accurate and reliable sensing readouts. This strategy can similarly offer an effective solution to overcome the limitations of the CNT-based sensor baseline drift.

CNT-based chemiresistive sensors that are incapable of fast response and recovery times may not be appropriate for applications with rapidly fluctuating analyte concentrations, such as real-time monitoring of hazardous gas leaks or detection of trace vapours under convective atmospheric conditions[21]. To enhance sensor kinetics, heating elements can be incorporated to provide additional energy to accelerate both the response and reset rates[184,185]. However, the appropriate temperature range will generally be limited because of the metastable nature of most non-covalent functional schemes and CNTs are prone to oxidation at elevated temperatures in air.

To ensure accurate and reliable performance of persistent CNT-based chemiresistive sensors, repeated calibration may be necessary to account for baseline conductance drift resulting from environmental induced and intrinsic ageing. Large drifts in CNT conductance can confound sensor readouts and may also lead to reductions in sensor sensitivity[21,227]. The low cost of CNT sensors enables the frequent renewal of the sensor with fresh chemiresistive elements. Although it remains to be seen, it is assumed that commercially produced CNT sensors can be reproducibly produced such that they may not need calibration when used for only short durations (less than 1 day). If the sensors are needed to be persistently operative for long periods, additional effort and resources may be required to maintain accuracy in CNT-based chemiresistive sensors.

When the dynamic range of CNT-based chemiresistive sensors is limited, there will be barriers to their applicability in scenarios that require measurement of an analyte over broad concentrations. Moreover, CNT-based chemiresistive sensors sometimes exhibit a nonlinear response to the target analyte across the concentration range[67,95]. This nonlinearity can pose challenges in the accurate quantification of analyte concentrations. In particular, the chemiresistive response may reach saturation at elevated analyte concentrations, leading to a plateau in the sensitivity of a sensor[67,95]. Saturation effect can compromise the ability of a sensor to accurately differentiate between various high-concentration levels of the target analyte, thus restricting its utility in applications in which high concentrations of analytes and interferents are expected. The latter limitation may be mitigated by using a sensor array wherein different chemiresistive formulations have varying sensitivities to the analyte. The intrinsic interaction between the CNT selector and the target analyte governs this nonlinear behaviour, the development of multiple synergistic CNT functionalization strategies can expand the dynamic and linear range of the sensors.

Outlook

The practical development of CNT-based chemiresistive sensors faces several challenges, such as inconsistencies in sensing performance resulting from variations in CNT quality, purity, defect levels and device fabrication[31]. High-purity CNTs with specific sizes or chiralities are difficult to access because of inefficient separation methods that lack scalability. Consequently, developing robust and selective CNT synthesis and isolation methods suitable for large-scale sensor fabrication processes remains a crucial and largely unmet need. Furthermore, the cost of fabrication can also present a barrier to the adoption of more advanced CNT-based sensors when compared with the less-expensive metal oxide alternatives. It is possible to overcome these challenges through alternative approaches, such as CVD of selectors or the direct growth of CNTs on the device[256]. This approach enables the direct integration of sensing and electrode materials, albeit at the expense of a more complicated fabrication process and limitations in the device substrates. Establishing uniform and robust contacts between sensing and electrode materials is essential for ensuring sensor stability and reproducibility.

The development of chemical sensors for health monitoring is a highly promising area of research, and there is an increasing demand for personalized health care and real-time, continuous monitoring of physiological parameters[9,143,257]. However, the integration of electronic devices with soft biological tissues or wearable garments presents challenges such as low biocompatibility and conformability to irregular surfaces. Flexible and stretchable electronics consisting of elastomers such as hydrogels have emerged as a potential solution, in which CNTs have been demonstrated to be effectively incorporated as structural mechanical elements with electronic properties[257–259]. Improved compatibility and adaptability will expand the scope of CNT-based chemical sensors.

Although CNT-based chemiresistive sensors have the capability to detect analytes at low concentrations, they often encounter limitations in selectivity to distinguish between analytes in complex environments[21]. Sensor arrays composed of multiple sensing elements that respond differently to a single analyte can generate distinctive fingerprints for the analyte to enable its identification and classification[28,260]. Effective sensor arrays require sensor elements that have very different, or ideally orthogonal, responses to analytes[261]. Uncorrelated drift between sensor elements can also confound a sensor array, and hence sensor stability is extremely important. The integration of FET capabilities in a sensor array could boost its power in resolving and identifying analytes in complex environments and provide large data sets amendable to machine learning analysis. However, the elaborated FET sensors also increase fabrication cost and require more complex electronics than a simple two-electrode chemiresistor. Novel CNT FET device architectures have been developed to incorporate a high density of CNT-based transistors for scalable fabrication[262]. Machine learning algorithms are likely to find utility in detecting and correcting drifts and deconvoluting complex signals from chemiresistive sensor arrays. The machine learning algorithms and other analytical techniques, including artificial neural networks and principal component analysis, can determine unique fingerprints for each set of analytes with a sensor array[260,263].

This Primer has detailed the fundamentals of CNT-based chemiresistive sensing, ranging from CNT functionalization, sensing mechanism, device architectures, fabrication methods, performance parameters, strategies for enhancing sensor selectivity, methods for increasing sensitivity to the limitations of methods to data reproducibility. The utility of CNT-based chemiresistive sensing is illustrated through examples from the literature, showcasing applications in environmental monitoring, food and agricultural safety, national security, biological sensing and health diagnostics. Despite the persisting challenges, innovative solutions from the scientific community are rapidly advancing new generations of practical, sensitive, selective and robust chemical sensors. This introductory Primer intends to expedite the adoption, implementation and advancement of this technology, ultimately facilitating the availability of commercial CNT-based chemiresistive sensors in the near future for the betterment of safety and well-being of the society.

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