

Hindawi Publishing Corporation
Journal of Sensors
Volume 2009, Article ID 160698, 16 pages
doi:10.1155/2009/160698

Review Article

Carbon Nanotubes as Active Components for Gas Sensors

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Received 24 December 2008; Revised 30 March 2009; Accepted 13 April 2009

Recommended by Michele Penza

The unique structure of carbon nanotubes endows them with fantastic physical and chemical characteristics. Carbon nanotubes have been widely studied due to their potential applications in many fields including conductive and high-strength composites, energy storage and energy conversion devices, sensors, field emission displays and radiation sources, hydrogen storage media, and nanometer-sized semiconductor devices, probes, and quantum wires. Some of these applications have been realized in products, while others show great potentials. The development of carbon nanotubes-based sensors has attracted intensive interest in the last several years because of their excellent sensing properties such as high selectivity and prompt response. Carbon nanotube-based gas sensors are summarized in this paper. Sensors based on single-walled, multiwalled, and well-aligned carbon nanotubes arrays are introduced. Modification of carbon nanotubes with functional groups, metals, oxides, polymers, or doping carbon nanotubes with other elements to enhance the response and selectivity of the sensors is also discussed.

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1. Introduction

Carbon nanotubes (CNTs) are a group of one-dimensional nanoscale materials composed of carbon atoms with fullerene structure, in which each carbon atom is sp^2 hybrid and every carbon atom is covalently bonded to another three adjacent carbon atoms. According to the number of their wall layer, they can be single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). A single-walled carbon nanotube can be considered as being formed by rolling a piece of graphene to create a seamless cylinder with diameters of 0.4–2 nm. MWCNT comprise of several layers of graphene cylinders that are concentrically nested like rings of a tree trunk, with an interlayer distance close to that of graphite (0.34 nm). Both MWCNTs and SWCNTs have diameters in the range between fractions of nanometers and tens of nanometers and length up to several centimeters with both their ends normally capped by fullerene-like structures [1]. Three main methods being developed for CNTs synthesis are arc-discharge, laser ablation, and chemical vapor deposition (CVD) [2]. Since the discovery of MWCNTs [3] in 1991 and the SWCNTs in 1993 [4], CNTs have attracted extensive research interest due

to their outstanding structural, electronic, and mechanical properties such as unique tubular structure like fullerene, high chemical and thermal stability, low weight, high electrical conductivity, stability, good heat conductance, large surface area, flexibility, high elasticity, and, high mechanical strength. CNTs play very important role in nanotechnology which greatly influences many different disciplines involving biology, chemistry, physics, medicine, engineering, electronics and material science [5].

The electronic property of SWCNTs is determined by their size and chirality. The SWCNTs can be metallic or semiconductive. The conductivity of each layer of MWCNTs behaves like an SWCNT along the axial direction, while it is very poor between the layers. As a whole, most MWCNTs display good conductivity. The unique electronic property combining with others makes carbon nanotubes ideal building block for electronic devices such as quantum wires, diodes, field-effect transistors (FETs), sensors, and cold cathode field emitters [1].

Carbon nanotubes are attractive for the task of chemical sensors, especially for nanoscale gas sensors. The development of CNTs-based gas sensors has attracted intensive interest in the last several years because of their high response,

prompt response, low power consumption, small size and low operating temperature. The fabrication, structure and gas-sensing characteristics of CNTs-based gas sensors are reviewed in this paper and the challenge and strategic consideration for future development are also discussed. Gas sensors based on pristine CNTs including SWCNTs, MWCNTs and aligned CNTs are introduced, and the modification of CNTs with functional groups, metals, metal oxides and polymers for gas sensors are also discussed.

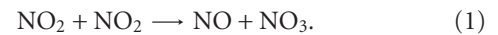
Most of the CNT sensors are based on FET devices with a semiconductive single nanotube (Figure 1(a)) or nanotube networks (Figure 1(b)) as the active sensing elements, and the conductivity of the CNTs was monitored when the sensors were exposed to various atmospheres.

2. Gas Sensors Based on Pristine Carbon Nanotubes

2.1. Gas Sensors Based on SWCNTs. It has been reported that SWCNTs are sensitive to NO₂, NH₃ and volatile organic compounds. The adsorption of gaseous molecules either donates or withdraws electron from the SWCNTs, leading to changes of electrical properties of the SWCNTs [6]. The high and fast response of the SWCNTs gas sensors has been assured. The drawback of these sensors is slow and incomplete recovery. To date, there have been a variety of attempts to overcome this limitation.

Kong et al. demonstrated the potential of CNT-based gas sensors when they reported the response of field-effect transistor (FET) devices to NO₂ and NH₃ [7]. The FET devices, utilizing a single semiconductive SWCNT (S-SWCNT) as the conduction channel, showed a unique response to NH₃ and NO₂ through chemical gating of the SWCNT. The response time of the devices to 200 ppm NO₂ was a few seconds, and the response (defined as the ratio between resistance after and before gas exposure) was approximately 100–1000. Recovery was slow at room temperature (ca. 12 hours), but decreased to approximately 1 hour upon heating. The response time to approximately 1% NH₃ was a few minutes with the response between 10 and 100. An individual nanotube sensor can be used to detect different types of molecules. The selectivity is achieved by adjusting the electrical gate to set the S-SWCNT sample in an initial conducting or insulating state. However, the mechanism causing the response of the FET based on single CNT remains unclear. Three models have been proposed to explain it. The first is charge transfer between the nanotube and the molecules adsorbed on its surface. The second is molecular gating of the CNT by the polar molecules such as NO₂, which results in shift of the gate threshold of the semiconducting SWCNT. The third is a change in the Schottky barriers between the nanotube and the electrodes [8, 9]. Peng et al. studied the adsorption, diffusion, and reaction of NO₂ on a SWCNT using *ab initio* simulations [10]. Since there are catalyst islands on SWCNT, and NO₂ molecules are known to interact with catalytic surfaces to form NO

and NO₃ molecules, a chemical reaction may occur as follows:



On the equilibrium, the desorption of NO₂ and NO molecules is very fast (less than 1 second at room temperature), while the desorption of NO₃ molecules is much slower (about 12 hours). From the fact that NO₃ is the major concentration on the SWCNT surface, and its recovery time will accordingly determine the recovery time of the overall SWCNT system, they deduced that it is NO₃ that is responsible for the slow recovery.

The different recovery rate can be interpreted in terms of the desorption energy barrier of gas molecules on the CNT. For FET devices, the desorption energy barrier for adsorbed dimethyl methylphosphonate [11], NH₃ [12], or NO_x [13] molecules on SWCNT could be reduced under positive gate voltages. A negative gate bias bends the energy band of the CNT upwards. Due to a thin barrier width, holes could tunnel through the barrier and enter the CNT channel easily. When a positive gate bias is applied, the CNT's energy band is bent downwards and hole tunneling is suppressed. A positive gate bias can promote fast recovery, which suggests that room temperature reversible CNT sensors for dimethyl methylphosphonate or NH₃ are feasible.

By simply casting of SWCNTs on an interdigitated electrode, Li et al. [14] fabricated a gas sensor for detection of gases and organic vapors at room temperature. The sensor responses are linear for concentrations of sub ppm to hundreds of ppm with detection limit of 44 ppb for NO₂ and 262 ppb for nitrotoluene. The recovery time was very long, on the order of 10 hours because of the higher bonding energy between SWNTs and NO₂. By using ultraviolet (UV) light to knock the adsorbed molecules out of the SWCNT sites, the recovery time was shortened to about 10 minutes. The UV exposure decreases the desorption-energy barrier to ease the NO₂ desorption. Under UV illumination, oxygen photodesorption causes a reduction of the hole carriers in the SWCNT, thus lowering the conductance of the sample. In air, gradual oxygen re-adsorption onto the nanotube upon turning off the light leads to the recovery of sample conductance [15].

Efforts have also been made to improve gas desorption by heating the sensors and increasing the flux rate of carrier gas. Quang et al. fabricated sensors from SWCNTs by a screen-printing method [16]. These sensors have been exposed to NH₃ gas at room temperature with nitrogen as the carrier gas. The SWCNTs are very sensitive to NH₃ and can detect NH₃ with low concentration of 5 ppm with a response time of 10 minutes. When the sensor is exposed to NH₃, electrons are transferred from NH₃ to SWCNTs. NH₃ donates electrons to the valence band of the carbon nanotubes, decreasing the number of holes, thereby increasing the separation between the Fermi level and the valence band. This forms a space charge region at the surface of the semiconducting SWCNTs, which increases

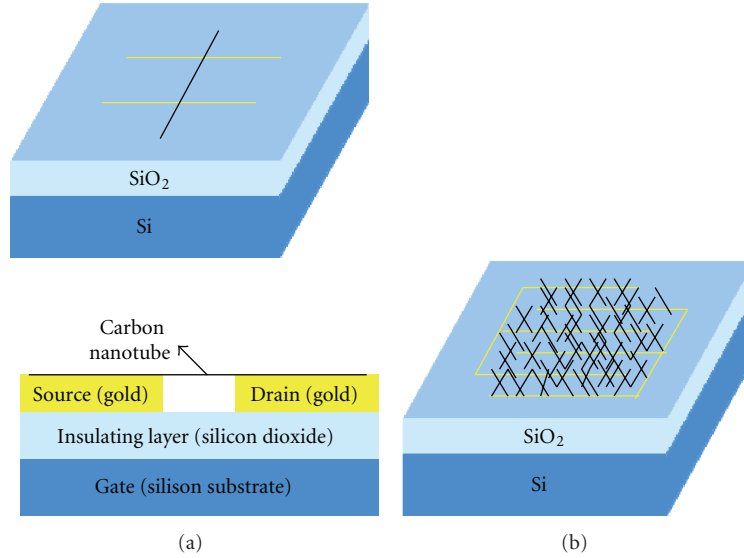


FIGURE 1: Schematic diagrams of (a) a gas sensor based on FET with a single carbon nanotube as sensing element, and (b) a resistive gas sensor with CNT bundles or thin film as sensing element.

the electrical resistance. A saturation state is established at a concentration of about 40 ppm, and the response of the sensor continues to increase in conjunction with an increase in concentration levels. The sensor completely recovers to its initial state at 80°C and under 1000 sccm N₂ flux. Nguyen et al. also constructed sensors from SWCNT powders by screen-printing, followed by annealing pretreatment in open-air for 2 hours at various temperatures to enhance the sensor characteristics [17]. The sensor annealed at 200°C was employed for detection of NH₃ with 500 sccm N₂ flowing. After being exposed to 5 ppm NH₃ for 10 minutes at room temperature, the resistance of the sensor increased up to 8% in comparison with its initial value. The strong bonding between NH₃ molecules and the SWCNTs requires a long time to degas and it causes the slow recovery of the SWCNT-based sensor. The carrier gas flux was intensified in desorption time to remove the adsorbed NH₃ molecules from the SWCNTs. The stronger carrier gas flux was conducted, the better recovery the sensor exhibited. The behavior of the SWCNT shows a transition from semiconducting at a moderate temperature (<350°C) to metallic at high temperature (>350°C), which suggested that the heating treatment might cause a structural change in the SWCNT, leading to a change in its chirality. Heating at a moderate temperature could reduce the resistance of the sensor, therefore degrading response in detection of NH₃. In order to avoid this problem, heating was not applied in sensing duration but in desorption time, for only 5 minutes at 70°C. In addition, the carrier gas flux was maximized to 1000 sccm for degassing. In summary, by increasing the carrier gas flux, combined with heating at 70°C, the sensor recovery was dramatically improved. All these methods improved partly the recovery of the SWCNTs-based sensors, but the recovery time is still not satisfactory.

According to the thermodynamics, the adsorption or desorption rate of gas molecules on solid surface could be expressed as follows:

$$\begin{aligned} r_a &= K f(\theta) \exp\left(-\frac{E_a}{RT}\right), \\ r_d &= K' f'(\theta) \exp\left(-\frac{E_d}{RT}\right), \end{aligned} \quad (2)$$

where r_a and r_d are the rate of adsorption and desorption, respectively; E_a and E_d are the activation energy of adsorption and desorption, respectively; T is the temperature; K and K' are the adsorption or desorption rate constant. θ is the fraction of the surface occupancy. $f(\theta)$ is a function related to surface vacancy ($1 - \theta$), $f'(\theta)$ is a function related to generally written to be related to surface occupancy (θ). Based on the above equations, r_a increases with the increasing of the gaseous pressure and fraction of the surface vacancy and reduces with the increasing of the adsorption activation energy. r_d increases with the increasing of the desorption temperature and fraction of the surface covered and reduces with the increasing of the desorption activation energy. As a result, heating is favorable for desorption, thus enhancing the recovery of the sensors. On the other hand, irradiation with UV light reduces the desorption activation energy, which is plausible for recovery of the gas sensors also.

2.2. Gas Sensors Based on MWCNTs. So far, it has been reported that MWCNTs are sensitive to a variety of gases such as NH₃, NO, NO₂, H₂, SF₆, and Cl₂. The main drawback of MWCNTs gas sensors is also the slow recovery. For example, Varghese et al. [18] investigated two sensor geometries, one capacitive with MWCNT-SiO₂ composite placed over a planar interdigital capacitor, the other resistive with MWCNTs

grown upon a serpentine SiO₂ pattern. Reversible behavior is demonstrated for the MWCNTs sensors in response to humidity, CO and CO₂. The response time of both sensors to NH₃ was approximately 2-3 minutes but it took the sensor several days in vacuum at 100°C to recover the original response. The impedance changes are attributed to p-type conductivity in semiconducting MWCNTs, and the formation of Schottky barriers between the metallic and semiconducting nanotubes. Of the sensors tested, the interdigital capacitor showed higher response. Nguyen et al. [19] developed a device with interdigital Pt electrodes on an Al₂O₃ substrate in order to evaluate the MWCNTs-based gas sensor capabilities. The MWCNT films were found to exhibit a fast response and a high response to NH₃ at room temperature. The response ($S = (R_0 - R)/R_0$, where R_0 represents the resistance in dry air and R is the resistance in the NH₃ gas environment), varies from 75% to 85% when the gas concentration increases from 2500 to 7500 ppm. This change is due to the electron transfer from gas molecules to the nanotubes, leading to decrease of the resistance of the CNTs film. Moon et al. [20] fabricated the sensor employing MWCNTs as an active sensing element by using screen-printing method, and the sensor returned to the initial conductance employing a bias voltage for detecting NO₂. The response ($S = G_g/G_0$, where G_0 is the initial conductance of the sensor and G_g is the conductance of nanotube films being exposed to NO₂) to 50 ppm NO₂ was approximately 22.7%. In a vacuum state, the sensor conductance was refreshed using a CNT-bias-heating method. The recovery was maintained for 10 minutes with bias voltage of 10 V, and the heating value was 28.8 cal. The recovery time decreased when the degassing energy was provided all at once, more than the divided heating. MWCNT films in the sensor could be used as a heater with a bias voltage, and the recovery time could be controlled by a bias voltage. The temperature variation was dependent on the bias voltage and the possible high electrical current. Gas desorption is affected by heating value which is controlled by time and bias voltage. The recovery time decreased upon an increase of bias voltage.

Suehiro et al. [21] demonstrated the partial discharge detection in SF₆ gas using an MWCNTs-based gas sensor. The sensor was fabricated by positive dielectrophoresis of MWCNTs on a microelectrode array. The sensor can detect main decomposition products such as SO₂ or HF at ppm level. When the partial discharge was generated, the electrical conductance of the MWCNT sensor gradually increased. The sensor response was reversible and was influenced by both the partial discharge intensity and the relative position of the sensor to the point electrode. The increase of the sensor conductance was caused by an electronic interaction between MWCNTs and nonidentified oxidative decomposition products. The sensor could realize a real-time detection of faint partial discharge activities that detection tubes could not sense.

An electrochemical gas sensor modified with MWCNTs film as electrocatalyst for the determination of Cl₂ has also been constructed [22]. Cl₂ gas was allowed through the cathode surface of the sensor, and the resulting galvanic effects were monitored. This amperometric gas sensor showed

excellent response, high stability, and fast recovery for the determination of Cl₂ in H₂SO₄. In the plateau potential region, the reduction of Cl₂ is controlled with the mass transfer of Cl₂ through the working electrode. Therefore, the limiting current produced in this region can be used to quantify the Cl₂ concentration. When using nanotube-based microelectrode, the electrode has a porous structure and is probably well wetted by the solvent/electrolyte medium [23]. The performance of the electrochemical sensor for Cl₂ with MWCNTs as electrocatalyst was stable and it was not interfered by the redox gases, such as CO, NO, O₂, CO₂, and C₃H₈. CO₂ is an inert gas, so it is difficult to react on the surface of MWCNTs-modified electrode. The response and recovery time of this sensor is about 150 seconds. The response time for MWCNTs is prolonged to about 150 seconds due to the small proportion of exposed edge plane.

As mentioned before, SWCNTs consist of single graphite sheets, while MWCNTs comprise an array of nanotubes that are concentrically nested. Depending on their chirality and diameter, an SWCNT can be either metallic or semiconducting. In practice, it is difficult to obtain only semiconducting nanotubes from grown samples, which are usually mixtures of both metallic and semiconducting SWCNTs [24]. Suehiro et al. [25] demonstrated that the normalized response of the SWCNT sensor was higher than that of the MWCNT sensor. Probably it is because SWCNTs contained more semiconducting tubes. In general, MWCNTs show a conducting (metallic) behavior at room temperature. However, MWCNTs could contain some semiconducting tubes among predominantly metallic ones. The higher normalized response of the SWCNT sensor may be attributed to higher abundance of the semiconducting tube, which is responsible for the sensor response.

2.3. Gas Sensors Based on Well-Aligned CNTs. It has been reported that aligned CNTs (ACNTs) are sensitive to NO₂, NH₃ and H₂. For example, Valentini et al. [26] prepared aligned CNT thin films by pulsed plasma chemical vapor deposition system for the detection of NO₂. The sensors exhibited fast and high response at room temperature and could detect as low as 10 ppb NO₂ at 165°C with fast recovery. The resistance of CNTs films decreased while contacting with NO₂, whereas it increased with NH₃, ethanol, humidity, and C₆H₆. The CNT film can be viewed as an aligned network of CNTs somewhere connected with CNT/CNT junctions. The crossed junctions between CNTs act as a gate for carriers to move in the film, and they may consist either in directly cross-linked defective nanotubes or in amorphous carbon impurities. Therefore the CNT film can be represented as a network of effective resistors formed by the resistance of the nanotube body, the resistance of the junctions, and the tunnelling resistance due to tube-tube electronic coupling between adjacent but not connected nanotubes. At 165°C, NO₂ is favored to decompose O₂ molecules in the air, generating atomic oxygen which preferentially attacks the defective sites of the CNT, thus produced volatile species like CO and CO₂ with the consumption of the defective sites. Moreover, amorphous carbon impurities

were also oxidized in such conditions, thus decreased the number of metallic like (Fermi) junctions. Cho et al. [27] fabricated a sensor by using selectively grown MWCNTs as the sensing element on a substrate of a stacked microheater structure with a Cr heater and a diaphragm to improve the recovery time and response of the MWCNTs films. To offer more reaction area between MWCNTs and NO₂ molecules, MWCNTs' films with mesh and serpentine shapes were fabricated. It took about 6 hours for the sensor to return to the initial resistance at room temperature. The MWCNTs thin films can be better recovered only by properly selecting the thermal treatment protocols. The change of the resistance of the mesh-shaped MWCNTs films to NO₂ was found to be larger than that of the serpentine-shaped MWCNTs films because the number of reaction areas between MWCNTs and NO₂ molecules was increased. Ueda et al. [28] prepared well-aligned CNTs on Si substrate by thermal CVD. The resistance of the sensor decreased with an increase of ambient NO and NO₂ gas concentration. The CNTs thin film can be applicable to an NO_x gas sensor. The changing rate of the resistance of the sensor was proportional to the concentration of the target gas. UV light irradiation can reset the resistance of the CNTs sensor by photodetachment of adsorbed molecules at room temperature. Hoa et al. [29] developed a vertical transport type CNTs-based NH₃ gas sensor structure. The structure features regular arrays of CNTs with uniform diameter and length, but the nanotubes also have high defect levels. The sensor shows high response, fast response time of less than 1 minute and good reproducible recovery behavior in atmospheric pressure with the forward biases of 5 V at room temperature due to the high defect density, and could detect NH₃ at the range of 0.1–6%. The CNTs with a higher defect density revealed better response. The oxygenation degrades the response to NH₃, but the crystallographic defects can enhance it in the CNT sensors. The recovery time is not sensitive to the gas concentration, which may be due to the forced desorption of the NH₃ molecules by the refreshing nitrogen flow. Figure 2 shows the schematics of sensor fabrication process and switching of the sensor measured at different NH₃ concentration. The regularity of the CNTs in diameter and length was a great help in clearly defining the sensors' specification and in realizing sensor-to-sensor uniformity.

N₂ absorption characteristics of the vertically aligned CNTs-based three-terminal gas sensor at room temperature were also studied [30]. Upon exposure to N₂ (filling pressure from 50 mTorr to 500 Torr) and without N₂ at 10 V bias voltage, the electrical resistance of the as-made devices was found to increase and to return back, respectively. Compared to a low bias, a high drain-source voltage enhanced the response for monitoring N₂ gas. N₂, owning higher adsorption energy, was easier to absorb by CNTs than Ar. The response was further improved by applying a negative gate voltage owing to the addition of conducting holes to the CNTs mat.

The response of multifinger with aligned SWCNT is double with respect to disordered SWCNT [31]. This effect is probably induced by the fact that the ordered SWCNTs are more uniformly exposed to the NH₃ molecules, than the case of placement of SWCNTs in form of a random network,

in which part of the SWCNT remains inaccessible to the gas molecules.

Gas-sensing performance of pristine CNT sensors is summarized in Table 1.

3. Gas Sensors Based on Modified Carbon Nanotubes

3.1. Gas Sensors Based on CNTs with Functional Groups.

Modification of CNTs with functional groups, metal nanoparticles, oxides, and polymers will change the electronic properties of them, and enhancing the selectivity and response to specific gases though the interaction of the target molecules with the functional groups or additives is very different. Most of the previous reports are based on utilization of carboxylic acid (–COOH) group, which provides reactive sites for interacting with different reactive compounds, at the ends and side-walls of the CNTs. Hsu et al. [32] reported that the –COOH group grafted on MWCNTs provides reactive sites via esterification or elimination, and the MWCNTs retain the graphitic structure. The HCl-treated MWCNTs were efficiently oxidized with nitric acid/hydrogen peroxide ($v/v = 2/1$) solution to generate –COOH group on the defect sites of MWCNTs. The surface acoustic wave (SAW) crystal sensor coated with MWCNT–COOH/poly(*n,n*-dimethylamino propylsilsesquioxane) exhibited a high response for ethanol vapor efficiently. Mäklin et al. [33] demonstrated NO gas sensing with carboxyl functionalized SWCNTs and MWCNTs. When exposed to NO, the conductivity of the sensors changed up to about 40% for SWCNTs and 12% for MWCNTs; however, the response was found to be fairly independent on NO concentration. Sensors made of SWCNTs outperform their counterparts with MWCNTs, which is a sign of tunable Fermi level in the semiconducting nanotubes. Recently, Fu et al. [34] demonstrated experimentally that sensors made of carboxylated SWCNTs were sensitive to CO, with a lower detection limit of 1 ppm, whereas pristine SWCNTs did not respond. The authors exploited the different responses of carboxylated and pristine SWCNTs to differentiate between CO, NO, and NO₂. The COOH functionality is crucial to the CO sensing, and the CO molecules can be absorbed on carboxylic acid functionalities through weak hydrogen bonding.

Tran et al. [35] investigated the effect of –NH₂ functionalized SiO₂ surface on the gas sensing properties of SWCNTs modified with 3-aminopropyltriethoxysilane (APTES). The relative resistance change of the SWCNTs to NO₂ in the case of the APTES-treated surface was twice larger than the case without surface treatment under the same conditions. The surface treatment by the SWCNTs did not affect the recovery time of the gas sensor. A significantly fast response time of the sensor with the SWCNTs treatment was observed when exposed to 10 ppm or 50 ppm NO₂. The amine groups in the APTES monolayer, electron donating in nature, played a role of charge transfer to the semiconducting SWCNTs, and hence the amount of electrons transferred from SWCNTs to NO₂ molecules increased.

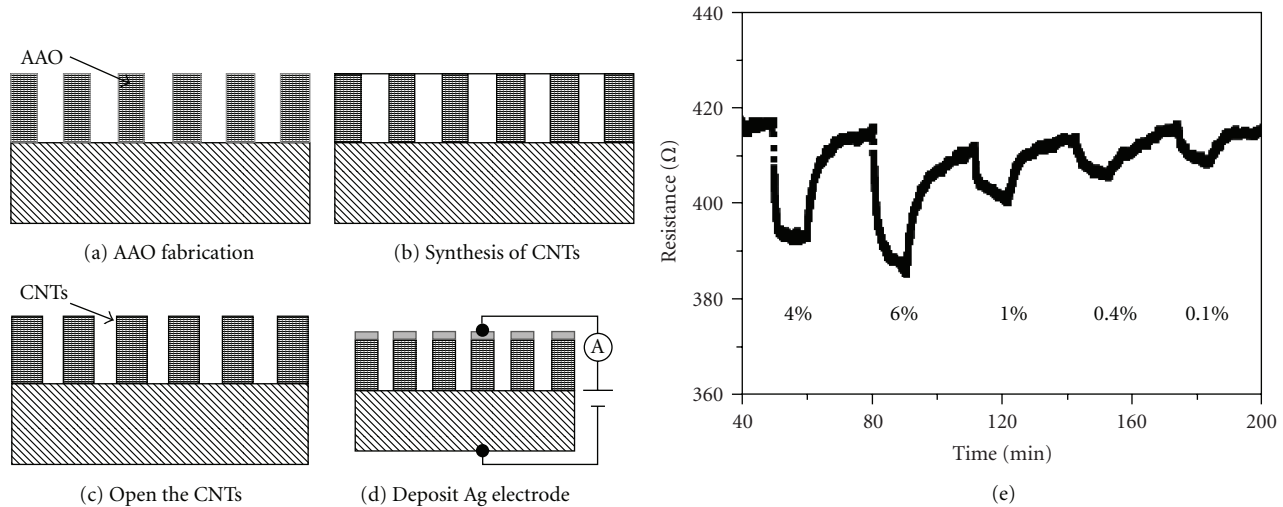


FIGURE 2: Schematics of sensor fabrication process. (a) Synthesis of anodic aluminum oxide (AAO) on p-type Si substrate, (b) synthesis of CNTs by thermal CVD, (c) removal of the top carbon layer by oxygen plasma, (d) Ag electrode deposition and (e) switching of the sensor measured at different NH_3 concentrations. Reprinted with permission [29].

TABLE 1: Summary of gas-sensing performance of pristine CNT gas sensors. (Note: N/S = Not-stated.)

CNT type	Sensor configuration	Targeted analytes	Detection limit	Response time	Recovery time	Reference
S-SWCNT	FET	NO_2 , NH_3	2 ppm NO_2 , 0.1% NH_3	<10 min	~1 h (200°C)	[7]
SWCNTs	Resistor	NO_2 , Nitrotoluene	44 ppb NO_2 , 262 ppb Nitrotoluene	10 min	10 min (UV)	[14]
SWCNTs	Resistor	NH_3	5 ppm	~10 min	~20 min (80°C)	[16]
SWCNTs	Resistor	NH_3	5 ppm	~10 min	~10 min (70°C)	[17]
MWCNTs	Capacitor and Resistor	NH_3	10 ppm	2-3 min	several days (100°C in vacuum)	[18]
MWCNTs	Resistor	NH_3	2500 ppm	N/S	N/S	[19]
MWCNTs	FET	NO_2	50 ppm	~500 s	~10 min (10 V bias potential)	[20]
MWCNTs	Resistor	SO_2 , HF	10 ppm SO_2 , 4 ppm HF	N/S	N/S	[21]
MWCNTs	Electrochemical Gas sensor	Cl_2	100 ppm	~150 s	~150 s	[22]
ACNTs	Resistor	NO_2	10 ppb	~60 min	~60 min (165°C)	[26]
ACNTs	Resistor	NO_2	10 ppm	N/S	N/S	[27]
ACNTs	Resistor	NO , NO_2	2 ppm NO , 2 ppm NO_2	N/S	~20 min (150°C and UV)	[28]
ACNTs	Resistor	NH_3	~0.1%	N/S	N/S	[29]
ACNTs	FET	N_2	50 mTorr	N/S	N/S	[30]

3.2. Gas Sensors Based on Polymer Functionalized CNTs. Among the organic polymers, conducting polymers are the most promising materials for gas sensing as they have delocalized bonds that make them semiconducting or even highly conductive. Several conducting polymers, for example, polyaniline, polypyrrole, polythiophene have been demonstrated to be good sensing materials to function

at room temperature. They have been applied as conductometric, potentiometric, amperometric and voltammetric transducers for the detection of a wide variety of gas or vapors such as NH_3 , NO_2 , CO and VOCs. However, their selectivity and the environmental stability are poor. Recently, enhanced gas sensing by combining SWCNTs with organic polymers has been demonstrated. Qi et al. showed that

noncovalently dropcoating of polyethyleneimine (PEI) and Nafion (a polymeric perfluorinated sulfonic acid ionomer) onto SWCNTs FETs resulted in gas sensors with improved response and selectivity for NO_2 and NH_3 [36]. The PEI functionalization changed the SWCNTs from p-type to n-type semiconductors, and the sensors based on PEI modified SWCNTs were able to detect less than 1 ppb NO_2 with a response time of 1-2 minutes (defined as the time for 80% conductance change to take place) while being insensitive toward NH_3 . The conductance of the n-type multiwalled tube devices decreased upon NO_2 binding due to electron transfer to NO_2 reducing the majority carriers in the nanotubes. This NH_3 insensitivity is attributed to low binding affinity and sticking coefficient of NH_3 on the electron-rich (due to high-density amines on PEI) n-type SWCNTs. PEI functionalized SWCNTs are highly selective to many other molecules including CO , CO_2 , CH_4 , H_2 , and O_2 . The sensor recovery was done by desorbing NO_2 with UV light illumination. Contrary to PEI-coated sensors, Nafion coated SWCNTs were insensitive to NO_2 but exhibiting a good sensitivity toward NH_3 . Chemical functionalization of SWCNTs with covalently attached poly-(m-aminobenzene sulfonic acid) (PABS) has been demonstrated to have better sensing performance toward NH_3 and NO_2 than simply carboxylated SWCNTs. Bekyarova et al. reported that the SWCNTs-PABS devices showed significant sensitivity to 5 ppm NH_3 owing to PABS deprotonation during NH_3 exposure [37]. This deprotonation resulted in hole depletion from the SWCNTs and a reduction in the overall conductance of the SWCNTs-PABS system. Zhang et al. used SWCNTs-PABS devices to reach detection limits of 100 ppb NH_3 and 20 ppb NO_2 with short response time and full recovery [38]. At 20–30°C, SWCNTs-PABS sensors usually take several hours to regenerate after exposure to NO_2 above 300 ppb. Sulfonic acid groups as dopants play an important role in balancing the charge distribution within the polymer, and they are especially attractive for introducing acid-base response. When PABS is exposed to NH_3 or water vapor, the adsorbed molecules cause deprotonation of the polymer, which depletes hole carriers and thus resulting in an increased electrical resistance. In contrast, exposure to NO_2 causes protonation of the polymer, which induces hole accumulation and results in a decreased resistance of the SWCNT-PABS sensors. When the sensor is purged with reference gas, the process is reversed and the original electrical resistance is restored.

CNTs have also been incorporated into polymers to form nanocomposites, which are usually casted to thin films and serve as sensing elements. For example, polypyrrole (PPy)/SWCNTs nanocomposite-based gas sensors have been fabricated by using a chemical polymerization technique followed by spin-casting onto prepatterned electrodes [39]. The response of the nanocomposites was about ten times higher than that of PPy (the resistance changed about 6% at 200 ppm NO_2). The response was recovered fully after about 2 hours in the first cycle. However, in the next cycles, not only the response was degraded, it was also not fully recovered. The SWCNT bundles could be nanodispersed, which may increase the specific surface area of the coated

PPy and thereby increase the response further. The recovery time could be shortened, particularly in the nanocomposite, by taking advantage of the Joule-heating effect. Liu et al. synthesize individual SWCNT/PPy composite nanocables based on nanotube FET [40]. A recovery in conductance was observed with nanotube/PPy nanocables upon further deposition of PPy, which results from the conduction through the conducting PPy layer. Furthermore, these composite materials enhanced conductance upon NO_2 exposure and reduced conductance upon NH_3 exposure. The observed conductance suppression in nanotube/PPy nanocables may originate from several factors. The first is the formation of scattering centers close to the nanotube when PPy was deposited. The deposited PPy might form covalent bonds with the nanotube at the defect sites and subsequently lead to enhanced scattering. The PPy coating may significantly alter the Schottky barrier at the metal-nanotube contacts and contribute to the observed conductance suppression. Santhosh et al. developed an amperometric sensor based on polydiphenylamine (PDPA) grafted MWCNTs (MWNT-g-PDPA) for determination of CO . Cyclic voltammetry is used to fabricate the modified electrode and to demonstrate the electroactivity of MWNT-g-PDPA-ME toward gaseous CO . The sensor exhibited high response for oxidation of CO in a 0.5 M HClO_4 solution [41]. The sensor showed excellent linear concentration range between 10 and 200 ppm (correlation coefficient $r = 0.9941$) with a substantially low detection limit of 0.01 ppm. The response to CO was rather quick; time for 96% response and 98% recovery to 100 ppm CO was about 2 and 3 seconds, respectively. The oxidation of CO to CO_2 occurred at the triple-phase boundary among the electrolyte, MWNT-g-PDPA-ME and CO . When the MWNT-g-PDPA-ME was coated with 0.5% Nafion, the interference from NH_3 , CH_4 , C_3H_8 , and N_2O (500 ppm) was not detected at MWNT-g-PDPA-ME. The insignificant or noninterference from these gases is attributed to the solubility and dielectric properties of the gases at a fluorinated polymer. Long-term stability of the MWNT-g-PDPA-ME was checked for 10 days, and no change in the sensing current was observed.

Modification of CNTs with polymers also improves their sensing properties toward vapors of organic compounds (VOCs). Abraham et al. developed a compact wireless gas sensor based on an MWCNTs/PMMA composite chemiresistor [42]. The composite film was made by ultrasonication of MWCNTs and PMMA (1 : 4 by weight) for 2 hours in dichloromethane, and the chemiresistors were fabricated by dip-coating. The sensor shows fast response (2–5 seconds) and 10^2 – 10^3 order increase in resistance upon exposure to dichloromethane, chloroform and acetone vapors. It returns to the initial level immediately after removing the gas. The sensing mechanism was explained by swelling of the polymer due to absorption of organic vapors into the PMMA and the charge transfer when polar organic vapors adsorb on the CNT surface. Solvents such as methanol, ethyl acetate and toluene, in which PMMA is insoluble or less soluble, also showed response. The polar nature of the solvents and the extent of interaction determine the response of the sensor. Methanol vapor which can form hydrogen

bonding with the polar groups on the CNT surface showed the maximum response among the three. However, this mechanism can induce only a weak response. Hexane is not a good solvent for PMMA. Being nonpolar, it did not show any response. The poly(3-methylthiophene)/MWCNTs nanocomposite-based sensor was used to selectively discriminate between chloromethane and methane, as the sensor showed a high response to chloromethane, while no response was observed when exposed to methane or many other VOCs [43]. The response and recovery time of the sensor was about 60 seconds and 30–45 seconds, respectively. The sensing mechanism was proposed to be based on ionization potential of the analytes. The nanocomposite sensor does not respond to vapors of acetone, acetaldehyde, benzaldehyde, tetrahydrofuran, methanol and ethanol. Zhang et al. fabricated the conductive polymer composites by in situ polymerization of styrene (PS) in the presence of MWCNTs or solution mixing of polystyrene with MWCNTs, respectively [44]. Compared with the composites prepared by solution mixing, the ones by in situ polymerization show much higher response to organic vapors over a wide range of MWCNTs (5–15 wt.%). Sorption of organic vapors into the polymeric phase of the composites leads to swelling of the matrix, expands the interparticulates' intervals and partially destroys the conductive networks. As a result, a drastic rise in resistivity of the materials is perceived. When the amount of MWCNT in the composites is low, tunneling effect contributes to conduction of the composites to a great extent besides the direct interfiller contacts. In the case of high MWCNT content, the excessive fillers inevitably resulted in aggregation of MWCNTs and broke the conducting paths. Only at certain optimized filler content, the conducting paths are mainly constructed by the bridged MWCNTs, which are easy to be broken down by the swelling of the matrix, and the vapor response reaches the maximum. The composites synthesized through polymerization-filling exhibit significant responsiveness to those organic vapors which are good solvents for the matrix, like tetrahydrofuran (THF), benzene, toluene, cyclohexane, carbon tetrachloride, chloroform, ethyl acetate and diethyl ether within short time of exposure, but low in response to those nonsolvents, such as alcohol. The resistance can be quickly and completely recovered to its original value as soon as the sample is transferred into air. Niu et al. constructed a highly selective gas sensor by chemical modification of MWCNTs containing carboxyl groups (MWCNT-COOH) with poly(ethylene glycol) (PEG) in the presence of N,N-dicyclohexylcarbodiimide (DCC) [45]. The MWCNTs grafted PEG sensor displayed high chemical selectivity, fast response and good reproducibility/high stability to chloroform vapor at room temperature. The resistance of the sensing film drastically increased over 10^7 within 1 second upon exposed to chloroform vapor. When it was transferred from the solvent vapor into dry air, the electrical resistance returned to the original value rapidly. This is attributed to the weak hydrogen bond interaction between chloroform vapor and polymers, which results in an abrupt adsorption of analyte molecules in a short time. The response of the MWNT-g-PEG system toward ethanoic acid and water is about 10^2 and 10^1 respectively, and only very

small response to any other solvent vapors was observed, and the film did not respond basically against nonpolar solvent vapors, for example, n-hexane.

Vertically aligned carbon nanotubes have also been modified with polymers for gas sensors. Valentini et al. fabricated a gas sensor by selective growth of aligned CNTs on $\text{Si}_3\text{N}_4/\text{Si}$ substrates patterned by metallic platinum [46]. The sensor was presented for inorganic vapor detection at room temperature. Poly(o-anisidine) (POAS) deposition onto the CNTs device was shown to impart higher response to the sensor. Upon exposure to HCl, the variation of the CNTs response is less than 4%, while the POAS-coated CNTs devices offer a higher response of 28%. The extended detection capability to inorganic vapors is attributed to direct charge transfer with electron hopping effects on intertube conductivity through physically adsorbed POAS between CNTs. Wei et al. developed novel multifunctional chemical sensors based on vertically aligned MWCNTs and polymer composites [47]. The sensors were fabricated by partially coating perpendicularly aligned MWCNTs with polymers, such as poly(vinyl acetate), polyisoprene, and then sputtering with gold electrodes. Rapid and reversible sensing of high concentrations of a variety of volatile organic solvents was demonstrated. The sensing mechanism was attributed to the charge transfer interaction with gas molecules and/or the intertube distance change induced by polymer swelling during gas adsorption.

Gas-sensing performance of polymer functionalized CNT gas sensors is summarized in Table 2.

3.3. Gas Sensors Based on Metal Nanoparticles Modified CNTs.

Metals exhibit a broad range of electronic, chemical and physical properties that are often highly sensitive to changes in their chemical environment [48]. They are mechanically and chemically robust and stable, hence, compared to polymer-based sensors, metal-based sensors can operate at higher temperature and in harsher environment.

Palladium is one of the most important metal catalysts for activation of small molecules such as H_2 . It is also used as active component in gas sensors, including CNTs-based gas sensors. Kong et al. demonstrated room temperature H_2 sensors based on Pd nanoparticles modified SWCNTs prepared by electron-beam evaporation deposition [49]. Pd-functionalized SWCNTs were shown to be highly sensitive toward H_2 , with 50% greater response of up to 50% relative resistance change to 400 ppm H_2 compared to bare SWCNT bundles. The response time was 5–10 seconds, and the time for recovery was about 400 seconds. It is well established that at room temperature, the adsorbed H_2 molecules on the surface of Pd nanoparticles are dissociated as hydrogen atoms, which dissolve into Pd with high solubility, leading to a decrease in the work function of Pd. This causes electron transfer from Pd to SWCNT and reduces the hole-carriers in the p-type SWCNT, and hence causes a decrease in conductance. The process is reversible as dissolved atomic hydrogen in Pd can combine with O_2 in air to form OH which will further combine with atomic hydrogen to form water and then leave the Pd-SWCNT system, thus

TABLE 2: Summary of sensing performance of polymer functionalized CNT sensors. (Note: N/S = Not-stated.)

polymer	CNT type	Sensor configuration	Targeted analytes	Detection limit	Response time	Recovery time	Reference
PEI, Nafion	SWCNTs	FET	NO ₂ , NH ₃	100 ppb NO ₂	~1-2 min	N/S	[36]
PABS	SWCNTs	Resistor	NH ₃ , NO ₂ , H ₂ O	20 ppb NO ₂ , 100 ppb NH ₃	1–10 min	Several hours	[38]
PPy	SWCNTs	FET	NO ₂	N/S	N/S	~2 h	[39]
PPy	S-SWCNT	FET	NO ₂ , NH ₃	100 ppm NO ₂ , 5 ppm NH ₃	N/S	N/S	[40]
PDPA	MWCNTs	Electrochemical gas sensor	CO	0.01 ppm	~2 s	~3 s	[41]
PMMA	MWCNTs	Resistor	dichloromethane, chloroform, acetone	N/S	2–5 s	~10 s	[42]
Poly(3-methylthiophene)	MWCNTs	Resistor	CH ₂ Cl ₂ , CHCl ₃ , CCl ₄ , CH ₄	N/S	60 s	30–45 s	[43]
polystyrene	MWCNTs	Resistor	the good solvents of PS	N/S	<4 min	~1 min	[44]
PEG	MWCNTs	Resistor	chloroform	N/S	<1 s	N/S	[45]
POAS	ACNTs	Resistor	HCl	100 ppm	N/S	N/S	[46]
poly(vinylacetate), polyisoprene, etc.	ACNTs	Resistor	Ethanol cyclohexane, tetrahydrofuran	N/S	<2 min	<2 min	[47]

recovering the sensor's initial conductance. Sayago et al. reported two different methods for the functionalization of SWCNTs with Pd for H₂ sensors [50]. The SWCNTs either being chemically functionalized with Pd or sputtered with Pd showed increased resistance when exposed to 0.1–2% H₂ at room temperature. The chemically functionalized Pd-SWCNTs sensors were superior to the sputtered ones. Both response time and response decreased with increasing temperature. However, only aged sensors provided good selectivity with minimum response to octane, toluene and ammonia in reversible and reproducible experiments performed at room temperature. This might be related to changes in the employed material, for example, introduction of carboxylic acid functionalities due to oxygen exposure, and/or to the complete removal of solvent residues, that might increase either the effective surface area or the hydrogen adsorption capabilities. Mubeen et al. developed a simple electrochemical functionalization method to fabricate a H₂ nanosensor by site-specific electrodeposition of Pd nanoparticles on SWCNTs [51]. Optimal sensing performance was obtained by varying the synthesis conditions (e.g., Pd electrodeposition charge, deposition potential and initial baseline resistance of the SWCNTs network). At room temperature, the optimized sensor showed good response toward H₂ (0.42% resistance change per ppm) with a detection limit of 100 ppm and a linear response up to 1000 ppm. The response time decreased from tens of minutes to a few minutes with increasing hydrogen concentration. The sensor's recovery time was shortened under humid air compared to dry air condition. Complete recovery was observed for the sensors at all tested concentration range and recovery time varied from 20 minutes at 100 ppm to

55 minutes at 1000 ppm. H₂ sensors based on SWCNTs decorated with Pd nanoparticles via a simple electrodeposition process on a flexible plastic substrate have also been demonstrated [52]. The Pd functionalized SWCNTs flexible sensors could readily detect 100 ppm H₂ (with 5% relative response) at room temperature. The response time for 37% of the steady state resistance change was in the range of a few seconds up to 1 minute, or close to 5 minutes to reach a value close to steady state. The typical flexible sensors exhibited response of ~75% for 0.05% hydrogen in air and response time of ~3 seconds for 1% hydrogen at room temperature. The mechanical bendability of the flexible sensors was proved to have negligible effect (<5%) on the sensing performance. Oakley et al. prepared SWCNTs films by a simple filtration process, subsequently coated with palladium [53]. The Pd-coated SWCNTs film could detect 10 ppm H₂ at room temperature and relative resistance change was about 20% for 100 ppm H₂ and 40% for 500 ppm H₂. The time for substantial recovery is less than 30 seconds when exposed to air and the power consumption is 0.25 mW. Ding et al. [54] fabricated robust CNTs-based hydrogen sensors with aligned CNTs grown in an anodic aluminum oxide (AAO) template. Without Pd modification, an Au-electrode CNTs sensor showed no response to H₂. A Pd-electrode CNTs sensor could detect H₂ (from 0.1% to 1.5% H₂) with a reversible response at room temperature. Typical response time of the Pd-electrode CNTs sensor is about 3-4 minutes. Furthermore, the CNTs grown in the AAO template were also demonstrated to be a good supporting material for nanoporous Pd film sensors. Typical response time of the CNTs-supported Pd film sensor is less than 7 minutes for dilute H₂, and less

than 4 minutes for medium concentration of H_2 . For the Pd-electrode CNT sensor, CNTs provide better contacts between the Pd-electrode and the substrate, while for the CNT-supported Pd film sensor, CNTs provide a better mechanical support and anchoring role so that the Pd film does not peel off easily after exposure to H_2 . The Pd film in the CNT-supported Pd film sensor mainly contributes to the total resistance of the sensor. Whereas, in the Pd-electrode CNT sensor, both the Pd film and the CNTs contribute to the total resistance of the sensor. Since the CNTs are less sensitive to hydrogen gas than the Pd is, less response has been found with the Pd-electrode CNT sensor than that with the CNT-supported Pd film sensor. SWCNTs coated with Pd nanoparticles by sputtering have been used to detect CH_4 ranging from 6 to 100 ppm. At room temperature, the Pd coated SWCNTs sensors give reproducible trends and consistently respond to heat and UV light for speed recovery [55]. A charge transfer sensing mechanism was proposed. Hydrogen atoms in CH_4 attract electrons from Pd, and electrons are withdrawn from the SWCNTs. This results in a weakly bound complex $Pd^{\delta+}(CH_4)^{\delta-}$, leaving more holes in the SWCNTs, thereby increasing the conductance of p-type or hole-occupied SWCNTs when exposed to CH_4 . Li et al. reported a composite of MWCNTs/Pd prepared by a facile method of chemical reduction exhibited a reversible and reproducible response magnitude of 4.5% toward 2% CH_4 at room temperature [56]. The response and recovery time was estimated to be 310 seconds and 176 seconds, respectively. The inert CH_4 does not undergo a charge transfer reaction with the MWCNTs to initiate a change in electrical properties, so MWCNTs alone are insensitive to methane. In the composite, the palladium nanoparticles undergo a weak interaction with the CH_4 molecules adsorbed on the composite to form a long range weakly bound complex $Pd^{\delta+}(CH_4)^{\delta-}$ at room temperature. The MWCNTs donate electrons to Pd^0 to promote the formation of the complex where CH_4 is electronegative. The hole density in the MWCNTs is thus increased, resulting in a higher current in the composite.

Carbon nanotubes have also been modified with other metals for gas sensors. Kumar et al. fabricated H_2 sensors based on MWCNTs functionalized with Pt or Pd by aqueous solution reduction of H_2PtCl_6 or $PdCl_2$ [57, 58]. They showed high response and reversibility at room temperature. The response time and recovery time are 10 minutes and 15 minutes for MWCNTs functionalized with Pt, respectively. Both the response time and recovery time are about 7 minutes for Pd-MWCNTs. The dissolved atomic hydrogen in Pt or Pd interstitials and the chemisorbed hydrogen on MWCNTs combine with oxygen in air, departing the Pt-MWCNTs or Pd-MWCNTs system in the form of water and thus recovering the sample electrical characteristics. Hydrogen sensing properties of Pd-decorated SWCNTs bundles and Pd-decorated exfoliated SWCNTs via Arabic gum treatment showed an improved hydrogen sensing behavior due to improved accessible surface area [59]. The response time and recovery time are 10 minutes and 14 minutes for Pd-exfoliated SWCNTs, respectively. The exfoliated SWCNTs are loosely bound and this results in an increase in accessible

surface area of SWCNTs which in turn decreases the time scale for the adsorbed hydrogen to escape from the sample surface. The resistance change in Pd-exfoliated SWCNTs is about 15%, which is more than doubled when compared with nonexfoliated Pd-SWNT (about 5%). Kamarchuk et al. demonstrated the effect of point heterocontact between SWCNTs and a gold microwire on the gas response [60]. Au-SWCNTs heterocontact sensors exhibit high response to NH_3 and NO_2 with fast response and relaxation and these two gases can be distinguished based on the direction of charge transfer between the analyte and the SWCNTs. The response time to 200 ppb NH_3 was 150 seconds, and the recovery time was 200 seconds. The mechanism of sensing is associated with formation of a thin conductive channel between Au and SWCNTs but the sign of the resistance change is controlled by the SWCNTs. Penza et al. demonstrated Au and Pt nanocluster functionalized MWCNTs chemiresistive sensors for NO_2 and NH_3 sensing at working temperature of 100–250 °C [61]. Au and Pt nanoclusters were sputtered on the surface of MWCNTs. The gas response of Pt- and Au-functionalized MWCNT gas sensors significantly improved by a factor up to an order of magnitude for NH_3 and NO_2 detection, respectively. The enhancement of the gas response of the metal-modified MWCNT sensors could be caused by a combination of two additional effects of (1) direct charge injection and (2) catalytically induced charge into functionalized MWCNTs. Espinosa et al. coated MWCNTs with Au or Ag nanoclusters deposited by electron beam evaporation [62]. The decorated MWCNTs' sensors were able to detect NO_2 at the range of 500 ppb–6.5 ppm at room temperature and significantly more selective than sensors based on MWCNTs without metal nanoclusters attached to their surface. The response of Au-MWCNTs sensors to NO_2 was higher than the one of Ag-MWCNTs. Both materials showed a reversible behavior after NO_2 exposure, provided that their operating temperature was raised to 150 °C in a flow of dry air. Upon adsorption of NO_2 gas molecules, there is a significant charge transfer between the metallic nanoclusters and the nanotubes, which results in a measurable change in the overall conductance of the active film. The decorated MWCNTs sensors were almost insensitive to CO, ethanol, or ethylene at concentrations up to 50 ppm.

Metal nanoparticle functionalized CNTs sensor arrays have also been reported. Star et al. fabricated gas sensor arrays by site-selective electroplating of Au, Pt, Pd, and Rh metals on isolated SWCNTs networks located on a single chip [63]. The difference in catalytic activities of the metal nanoparticles caused different selectivities for the detection of H_2 , CH_4 , CO, H_2S , NH_3 , and NO_2 . The output of the sensor array was analyzed using principal component analysis (PCA) and partial least squares regression (PLS) in order to identify the above-mentioned gases. Lu et al. demonstrated a gas sensor array composed of 32 sensing elements with pristine, metal-decorated (Pd, Au), and polymer-decorated SWCNTs for discriminating gases such as NO_2 , HCN, HCl, Cl_2 , acetone, and benzene at ppm levels [64]. CNTs-based technology holds the potential to excel in the design of arrays because the inherently small size of CNTs devices will allow for the integration of large numbers of functionalized

CNTs sensor elements that would show a unique response to numerous species.

Gas-sensing performance of metal functionalized CNT gas sensors is summarized in Table 3.

3.4. Gas Sensors Based on Nanostructured Oxides Modified CNTs. Metal oxide gas sensors have been investigated extensively since decades ago owing to their advantages of high response to pollutant gases, fast response and recovery, low cost, easy implementation, and small in size. However, they are usually operated at temperature range between 200 and 800°C. Sensors based on metal oxides (SnO₂, WO₃ or TiO₂) modified CNTs can detect gases such as NO₂, CO, NH₃ and ethanol vapors at low operating temperature with improved sensing properties.

Recently, sensors based on SWCNTs/SnO₂ nanocomposites with enhanced gas sensing performance have been reported. Wei et al. constructed SWCNTs/SnO₂ gas sensor by incorporating SWCNTs into a SnO₂ substrate. The fabrication involved heat treatment of the SWCNTs/SnO₂ layer, which was fabricated by spin coating using an organometallic solution dispersed with SWCNTs [65]. The prepared SWCNTs/SnO₂ nanocomposite sensors exhibit much higher response and recovery property in detecting NO₂ at room temperature than the blank SnO₂ sensor. The response time and recovery time are 9 minutes and 1.5 minute, respectively. A model is presented to relate potential barriers to electronic conduction in the hybrid material. This model suggests that the high response is associated with the stretching of the depletion layers at the grain boundaries of SnO₂ and the SWCNTs interfaces when detected gases are adsorbed. Gong et al. developed MEMS-based sensors integrated with nanocrystalline SWCNTs/SnO₂ sensing films realized by a polymeric sol-gel process [66]. The response of the SWCNTs/SnO₂ sensor is three times greater than that of the pure SnO₂ sensor with faster response and recovery in hydrogen detection. The response time and recovery time are 2–5 seconds and 3–5 seconds at the working temperature of 200 and 250°C, respectively. The working temperature has been reduced as low as 150°C. The greatly improved performance is attributed to the effective gas accessing nanopasses formed by SWCNTs. Hoa et al. fabricate an NH₃ sensor with a composite of SWCNTs and SnO₂ [67]. The sensor could detect the concentration of NH₃ down to 10 ppm at room temperature, and exhibited a fast response time of 100 seconds and recovery time of about 3.2 minutes. The SWCNTs in the matrix of SnO₂ provide the main conducting channels that effectively varies in its conductance upon adsorption of NH₃. The recovery time depends on the bonding force of NH₃ molecules to the SWCNT surface with respect to the desorption under nitrogen flowing. Thus, it can vary with the nitrogen flow rate.

MWCNTs have also been incorporated with SnO₂ for gas sensors with improved sensing properties. Liu et al. synthesized a compound material of MWCNTs coated with SnO₂ at ambient conditions [68]. The MWCNTs/SnO₂ sensor exhibited good sensing responses to liquefied petroleum gas (LPG) and ethanol (C₂H₅OH) vapor with fast response

and recovery within seconds at temperature of 335°C. Furthermore, the gas sensor response increased linearly with the increment of gas concentration of LPG and ethanol. The high response and low resistance may be attributed to the particular electrical transport mechanism. The resistance of the sensor is dominated by the barriers among the SnO₂ grains on the MWCNTs. Electrons travel through the SnO₂ grains into the MWCNTs, and then conduct in the MWCNTs with low resistance. Chen et al. synthesized MWCNTs/SnO₂ core/shell nanostructures by a simple wet-chemical method [69]. The thickness of the SnO₂ shell was about 10 nm and the diameters of the SnO₂ particles were 2–8 nm. Sensors based on the core/shell heterostructures exhibited enhanced ethanol sensing properties at working temperature of 300°C. The response to 50 ppm ethanol was up to 24.5, and the response time and recovery time were about 1 and 10 seconds, respectively. In addition, the fluctuation of the response was less than ±3% on remeasurement after 3 months. The enhanced ethanol sensing properties are attributed to the small size of the SnO₂ nanoparticles and the heterojunction of the core/shell structures of MWCNTs/SnO₂. Espinosa et al. demonstrated that the addition of a small quantity of oxygen-functionalized MWCNTs to metal oxides (SnO₂, WO₃ or TiO₂) can significantly improve the detection capability of metal oxides-based sensors at low operating temperature [70]. In particular, microsensors based on SnO₂/MWCNTs hybrid films operated at room temperature showed higher response towards NO₂ in the ppb range. TiO₂/MWCNTs sensors showed the lowest response to NO₂ and irresponsive to CO even at 150°C. The recovery time of the SnO₂/MWCNTs sensors was reduced from 45 minutes at room temperature down to 20 minutes at 150°C, while in the case of WO₃/MWCNTs sensors, the recovery time was reduced from 120 to 45 minutes. Furthermore, the response is fully reversible. A mechanism of response based on the development of two depletion layers, one at the surface of metal oxide grains and another at the interface of the n-metal oxide/p-MWCNT heterostructure, is postulated to be responsible for the improvement observed. Hieu et al. fabricated an SnO₂/MWCNTs composite-based NH₃ sensor by thin film microelectronic technique [71]. At room temperature, the optimal composite sensor exhibited much higher response and faster response recovery (less than 5 minutes) to NH₃ with concentration from 60 to 800 ppm, in comparison with the CNTs-based NH₃ sensor. The enhancement of the response to NH₃ of the composite sensors may result from the p-n heterojunction formed by CNTs and SnO₂ nanoparticles. The response of the MWCNTs/SnO₂ composite thin film gas sensor strongly depends on the preparation process of the sensitive film. The composite thin film with 15 wt% MWCNTs with diameter of 60–100 nm, the calcination temperature of 530°C under vacuum of 10⁻² Torr, and the film thickness of 400 nm are optimal conditions. The response of the sensor to NH₃ increases with increasing MWCNTs content and the composites using MWCNTs with the larger diameter show higher response because larger diameter MWCNTs would increase the number of gas molecules adsorbed on the

TABLE 3: Summary of sensing performance of metal functionalized CNT sensors. (Note: N/S = Not-stated.)

Metal	CNT type	Sensor configuration	Targeted analytes	Detection limit	Response time	Recovery time	Reference
Pd	S-SWCNT	FET	H ₂	<40 ppm	5–10 s (for half resistance change)	400 s	[49]
Pd	SWCNTs	Resistor	H ₂	1000 ppm	N/S	N/S	[50]
Pd	SWCNTs	Resistor	H ₂	100 ppm	10 min	20 min	[51]
Pd	SWCNTs	Resistor	H ₂	100 ppm	3–60 s (for 36.8% resistance change)	~5 min	[52]
Pd	SWCNTs	Resistor	H ₂	~10 ppm	<10 min	<30 s	[53]
Pd	ACNTs	Resistor	H ₂	100 ppm	<7 min	N/S	[54]
Pd	SWCNTs	Resistor	CH ₄	6 ppm	2–4 min	N/S	[55]
Pd	MWCNTs	Resistor	CH ₄	2%	~310 s	~176 s	[56]
Pt	MWCNTs	Resistor	H ₂	N/S	10 min	15 min	[57]
Pd	MWCNTs	Resistor	H ₂	N/S	7 min	7 min	[58]
Pt	MWCNTs	Resistor	H ₂ , NO ₂ , H ₂ O	N/S	~10 min	~14 min	[59]
Au	SWCNTs	Resistor	NH ₃ , NO ₂	<120 ppb NH ₃	150 s	200 s	[60]
Au, Pt	MWCNTs	Resistor	NO ₂ , NH ₃	100 ppb NO ₂ , 5 ppm NH ₃	N/S	N/S	[61]
Au, Ag	MWCNTs	Resistor	NO ₂	500 ppb NO ₂	~20 min	N/S	[62]
Pt, Pd, Sn, Rh	SWCNTs	FET	H ₂ , CH ₄ , CO, H ₂ S	N/S	~5 min	N/S	[63]
Pd, Au	SWCNTs	Resistor	NO ₂ , HCN, HCl, Cl ₂ , acetone, benzene	5 ppm	N/S	N/S	[64]

material. Increasing the annealing temperature may result in the improvement of the contact between SnO₂ nanoparticles and CNTs but the higher calcinated temperature may also result in burning of CNTs by residual oxygen or damaging of CNTs structure. An increase in thickness of the thin film composite sensors results in a decrease in the response due to the increase of the diffusion length of gases. Wang et al. reported a gas sensor based on SnO₂ doped with hydroxyl functionalized MWCNTs for detecting indoor formaldehyde [72]. The response of the MWCNTs-doped SnO₂ sensor was much higher than that of an undoped SnO₂ sensor. The lowest concentration of formaldehyde vapor detected by a 5 wt.% MWCNTs-doped SnO₂ sensor was 0.03 ppm. The response and recovery time of the sensor to 0.05 ppm formaldehyde vapor is about 100 seconds and 90 seconds at 250°C. The sensor response to formaldehyde is higher than to acetone, methanol, toluene, benzene and ammonia. High adsorption capacity of MWCNTs enhance the adsorption ability of the SnO₂ for formaldehyde molecules. Reducing molecules like formaldehyde act as temporary n-type dopants when they interact with CNTs, which leads to a decrease in resistance and hence to an increase in response of the MWCNTs doped SnO₂ sensor. The MWCNTs-doped SnO₂ material contains at least three kinds of interfaces, such as between SnO₂ grains, between MWCNTs, and between SnO₂ grains and CNTs (existence of a heterostructure). Bittencourt et al. demonstrated that WO₃ films impregnated with MWCNTs showed response to 500 ppb NO₂ under ambient conditions and 10 ppm NH₃ at 150°C, far below the typical operating temperature of WO₃ sensors [73]. Oxygen plasma functionalized MWCNTs were added to WO₃

by drop-coating deposition method. The adsorption at the surface of CNTs modifies the depletion layer at the n-WO₃/p-MWCNTs heterojunctions and this results in the modulation of the depletion layer at the surface of WO₃ grains. This change in the depletion layer at the n/p junction that induces change in the WO₃ matrix may explain the improvement in response shown by hybrid sensors.

The detection of acetone and NH₃ was found to be possible at ambient temperature with TiO₂/MWCNTs gas sensors fabricated by sol-gel method [74]. The TiO₂/MWCNTs composites obtained by Ti-isopropoxide route are reported as room temperature sensitive coatings. Sensing was highly reproducible in the composites, with fast adsorption/desorption cycles at room temperature. Composites based on as-received MWCNTs show an increase in films resistance during acetone and ammonia adsorption, while composites based on functionalized MWCNTs show longer acetone desorption time (300 seconds) and a decrease in resistance during ammonia sensing. Theoretical ab initio calculations predicted an inversion in the acetone → Ti_xO_y/CNT charge transfer direction as the size of the oxide cluster increases, explaining the inverse changes in resistance of the composites versus the components but have not been successful in explaining the differences observed in the composites during NH₃ adsorption. Detection of NH₃ might be also possible through the intertube modulation effect (i.e., MWCNT-TiO₂/NH₃-MWCNT junctions) and where titania is acting as a buffer layer to avoid MWCNTs dedoping. Llobet et al. fabricated resistive oxygen sensors based on TiO₂/MWCNTs hybrids by drop-coating method [75]. The hybrid layers based on TiO₂ and MWCNTs possess

TABLE 4: Summary of sensing performance of metal oxide functionalized CNT sensors. (Note: N/S = Not-stated.)

Metal oxide	CNT type	Sensor configuration	Targeted analytes	Detection limit	Response time	Recovery time	Reference
SnO ₂	SWCNTs	Resistor	NO ₂	N/S	9 min	1.5 min	[65]
SnO ₂	SWCNTs	Resistor	H ₂	300 ppm	2–5 s (200–250°C)	3–5 s (200–250°C)	[66]
SnO ₂	SWCNTs	Resistor	NH ₃	10 ppm	~100 s	~3.2 min	[67]
SnO ₂	MWCNTs	Resistor	LPG, C ₂ H ₅ OH	10 ppm	N/S	N/S	[68]
SnO ₂	MWCNTs	Resistor	C ₂ H ₅ OH	10 ppm	~1 s (300°C)	~10 s (300°C)	[69]
SnO ₂	MWCNTs	Resistor	NO ₂	100 ppb	N/S	20 min (150°C)	[70]
SnO ₂	MWCNTs	Resistor	NH ₃	60 ppm	<5 min	<5 min	[71]
SnO ₂	MWCNTs	Resistor	formaldehyde	0.03 ppm 500 ppb	100 s (250°C)	90 s (250°C)	[72]
WO ₃	MWCNTs	Resistor	NO ₂ , CO, NH ₃	10 ppm CO, 10 ppm NH ₃	N/S	N/S	[73]
TiO ₂	MWCNTs	Resistor	acetone, NH ₃	N/S	10–40 s (acetone)	10–300 s (acetone)	[74]
TiO ₂	CNTs	Resistor	O ₂	10 ppm	5–8 min (350–550°C)	~20 min (350°C)	[75]
SnO ₂ , TiO ₂	SWCNTs, MWCNTs	Resistor	C ₂ H ₅ OH	100 ppm	<10 s (210–400°C)	<10 s (210–400°C)	[76]

an unprecedented responsiveness toward oxygen (i.e., more than four times higher than that shown by optimized Nb-doped TiO₂ films). Furthermore, hybrid sensors containing MWCNTs respond at significantly lower operating temperature than their nonhybrid counterparts. These new hybrid sensors show a strong potential for monitoring traces of oxygen (i.e., <10 ppm) in a flow of CO₂. The heterostructure n-TiO₂/p-MWCNTs can be formed at the interface between titania and carbon nanotubes. Hybrid sensors are significantly more responsive to oxygen than pure or Nb-doped titania sensors because a slight change in the concentration of adsorbed oxygen at its surface can result in a significant change in the depletion layer at the n-TiO₂/p-MWCNT heterostructure. Duy et al. constructed SnO₂-TiO₂ and MWCNTs-included SnO₂-TiO₂ thin films by sol-gel spin coating [76]. The inclusion of MWCNTs at specific contents into the mixed oxides improved response of the sensor at low operating temperature (below 280°C). The response and recovery time of the sensors is less than 10 seconds at operating temperature of 210–400°C. The improvement of the gas sensor performance and the shift of operation temperature toward the lower temperature region can be attributed to the amplification effect of the p-n junctions in addition to the effect of the grain boundaries.

Gas-sensing performance of metal oxides functionalized CNT gas sensors is summarized in Table 4.

4. Gas Sensors Based on Heteroatom-Containing Nanotubes

Doping of SWCNTs with heteroatoms will change the electronic properties of the nanotubes, thus changing their

interaction with gas molecules and their sensing properties as well. Theoretical calculation predicted that SWCNTs doping with B, N, and so forth will enhance their sensing properties toward electron-rich or electron-scarce molecules. Pristine CNTs-based gas sensors are currently limited to sense gases such as NH₃, NO₂, SO₂, O₂, and NO. However, many highly toxic gases (such as CO and formaldehyde) cannot be detected using the pristine CNTs gas sensors. To improve gas-sensing performance, Peng et al. propose to use B or N doped SWCNTs, or composite B_xC_yN_z nanotubes as sensing element [77]. Using first-principle calculations, they demonstrated that these sensors can detect CO and water molecules, and more important, the response of these sensors can be controlled by adjusting the doping level of heteroatoms in a nanotube. Subsequently, Wang et al. investigated reactivities of the intrinsic and Al-doped SWCNTs with CO by density functional theory (DFT) calculations [78]. The Al-doped SWCNTs present high response to CO, compared with the intrinsic SWCNTs. Wang et al. [79] and Zhang et al. [80] investigated reactivities of B-doped SWCNTs with HCOH or HCN by using density functional theory calculations. Compared with the intrinsic SWCNTs, B-doped SWCNTs presents high response to HCOH or HCN. This is attributed to the strong chemical interaction between the electron-rich oxygen atom in HCOH or nitrogen atom in HCN and the electron-scarce boron atom of the doped SWCNTs. Bai and Zhou [81] investigated the adsorption of NH₃ and NO₂ in B- or N-doped SWCNTs by using density functional computations. The N-doping did not change NH₃ adsorption on SWCNTs but B-doped SWCNTs could be used for NH₃ sensing. Both B- and N-doping made NO₂ chemisorption feasible in SWCNTs but the binding of NO₂ with B was too strong, indicating an impractical recovery time as gas sensors.

5. Conclusion and Remark

Carbon nanotubes are active elements for sensing a broad variety of gases with high response because of their unique structure and electronic properties, and their rich configurations as well. Modification of carbon nanotubes with functional groups and metal nanoparticles or incorporation of carbon nanotubes with polymers and metal oxides will greatly enhance the selectivity of the carbon nanotubes-based sensors. CNTs-based gas sensors have proved to work well at room temperature, which reduces power consumption of the device and enables the safer detection of flammable gases. However, much effort has to be done before the practical application of CNTs-based gas sensors. Firstly, CNTs with defined structure and property need to be produced in large quantity at low cost. Secondly, the sensing properties, especially the selectivity and recovery, have to be improved. For practical application, gas sensors are required to be with high selectivity, low operating temperature, quick response and recovery. One common disadvantage of CNTs-based gas sensors is the potential interference from relative humidity at room temperature. Other main drawbacks are slow recovery and poor selectivity. There have been a variety of attempts such as heat treatment, ultraviolet light irradiation, increasing carrier gas flux, and modification of CNTs with functional groups or other additives to overcome the limitation. The instability of the CNTs in air at elevated temperature will limit CNTs-based gas sensors being operated at high temperature. CNTs-based gas sensors are sensitive to many gases or vapors such as NO₂, NH₃, H₂, CH₄, and Cl₂ at room temperature but the operating temperature of CNTs-based gas sensors for detecting O₂, C₂H₅OH, LPG, and formaldehyde is still relatively high. More efforts are needed on studying the long-term stability and reliability of the CNTs-based sensors, which has been less studied. Nevertheless, the discovery of carbon nanotubes, a group of outstanding nanomaterials, provides excellent candidates for gas sensors, especially for nanosensors which could be vital to their specific applications such as in space shuttles and satellites. Sensors based on single SWCNT FET, well-aligned CNTs structure for field emission devices, or electrochemical systems are the most promising devices for practical applications.

Acknowledgments

Financial support of the work by the Research Fund for the Doctoral Program of Higher Education (RFDP) under Grant 20070561008 and the Natural Science Foundation of China under Grant 20773041 is greatly acknowledged.

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