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Applications of Carbon Nanotubes and Their Polymer Nanocomposites for Gas Sensors

Dr. Abdul Hakim Shah

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Abstract

Because of extensive applications in industrial and environmental monitoring, biomedicines and pharmaceutics, etc., gas sensors are being focused widely by the research community since a few decades. Generally, gas-sensing materials include semiconducting metal oxides, vapour sensitive polymer, porous silicon, etc. Based on the gas-sensing principle of adsorption/desorption of target gas molecules on the sensors' surface, significant enhancement in sensitivity could be achieved by increasing the interfacial contact between the sensors' surface and analytes (target gases). Carbon nanotubes (CNTs), due to their unique electron transport phenomenon, have proven their ability to utilize them as sensing material in conductometric gas sensors. This chapter consists of three major sections. *First section* contains studies about the fundamentals of gas sensors and definitions of technical parameters used to characterize them. *Second section* describes up-to-date structural and chemical studies of the CNTs in detail in connection with the dependence of electrical transport phenomena upon these properties. Their gas-sensing mechanism and several literature reports about such investigations are also quoted and explained in easy language. *Third section* describes CNTs-polymer nanocomposites for conductometric gas sensors, which have been described in details and a comprehensive way. Conclusions have been drawn, and references are enlisted at the end of the chapter.

Keywords: CNTs, polymers, nanocomposites, gas sensors, sensing mechanism

1. Gas sensors; review

1.1. Criterion and their physical significance

Chemical sensors (gas sensors) are being intensely focused due to their extensive applications in industries, environmental monitoring, space exploration, food technology, biomedicine and

pharmaceutics. Their performance is characterized by several technical parameters such as sensitivity, lowest detection limit, response time, recovery time, selectivity and working temperature. Highly sensitive gas sensors are required for the leakage detection of explosive and toxic gases in industries. Gas sensors with quick response have strong demand in environmental monitoring and globe warming.

An effective gas sensor must have following decisive factors:

a. It must have high value of sensitivity magnitude and discrimination ability (selectivity).

b. It must have fast speed of responding.

c. It must have lower detection threshold value.

d. Its work temperature must be low for minimum power consumption.

e. It must be stable in repeating use.

In order to obtain above criterion, materials such as polymers, semiconducting metal oxides and silicon with high porosity are generally used. Taking in mind the principle of adsorption/desorption, maximization of the contact's cross-section between target gas molecules and gas-sensing material's surface is one of the major tactics to enhance the sensitivity magnitude.

Detection of different gases, particularly the volatile organic compounds (VOCs) such as ammonia, amines, ethanol and acetone, has vital significance in industries. *Ammonia* being pungent and toxic in nature is a by-product in industries such as fertilizers, refrigerant, as well as dung from agriculture, flora and fauna. Being a poisonous and explosive-nature gas, it could harm people at ppm or ppb level leakage. *Propylamine* ($C_3H_7NH_2$) is a high hazardous gas with caustic and exasperating nature; create pollution in chemical and fisheries industries. Similarly, in order to monitor alcoholic percent in the blood, *ethanol* sensing is necessary from the clinical and forensic point of view. *Acetone* is on high degree among all volatile organic compounds, which has applications as an organic solvent in the laboratories and industries. In the literature, there are recent investigations about its harmful internal as well as external effects on the health, for example, eyes' annoyance, sluggishness and sleepiness of the body nervous system when it is exposed to acetone continuously. In food technology, acetone is emitted by potatoes in their long-time storage. This shows that how much is it important to be detected timely [1, 2, 91].

The first gas sensor was designed by Seiyama in 1962, which was based on ZnO thin film with working temperature 400°C. Later on, several other material scientists contributed to this research area and their efforts took a big turn after the introduction of nanosized materials. Introduction of nanomaterials has made it more efficient to produce sensitive, selective, economic, small-sized sensing systems with low power consumption. Moreover, high surface area and hollow structure of the nanomaterials have exposed them effective for good adsorption. Therefore, nanomaterials such as carbon nanotubes (CNTs), metal oxides nanostructures (nanowires, nanofibres and nanoparticles) are under investigation for gas sensors.

1.2. Performance parameters for gas sensing

In the gas sensors research, in addition to the measurement of resistance (conductivity) or other physical properties, a set of characteristic parameters need to be evaluated for the performance prophecy of the materials [3]. A brief description of certain technical parameters as stated in the last section is presented as under.

1.2.1. Sensitivity

It is defined as 'the change of measured signal (response) of a gas sensor per unit change in analyte (target gas) concentration'. More specifically, 'it is the slope of a calibration graph'. As we know that the metal oxide-based gas sensors work on the principle of resistance change (so-called conductometric), therefore, their sensitivity is described in terms of change of resistance. Mathematically, we can write.

$$S^n_{red(oxd)} = R_{air(gas)} \Big/ R_{gas(air)} \tag{1}$$

$$S^p_{red(oxd)} = R_{gas(air)} \Big/ R_{air(gas)} \tag{2}$$

where the left hand sides of Eqs. (1) and (2) represent sensitivities of n-type and p-type semiconducting materials towards reducing and oxidizing gases, respectively. R_{air} is the base-line resistance of the sensor in air, and R_{gas} is the value of resistance when the sensor is exposed to the target gas. Some researchers do mention the % values of the sensitivities, which could be obtained by simply multiplying the right-hand side of Eqs. (4) and (5) by 100.

1.2.2. Selectivity

Selectivity determines the selective response of the gas sensor towards a specific target gas among a group of gases, or more precisely, the particularity of the gas sensor towards a specific target gas molecule in a mixture of gases. For example, for a mixture of target gases A, B, C and D, the selectivity of the sensor towards the target gas A is given as;

$$Sel_A = S_A \Big/ \sum S_i \tag{3}$$

where S_A denotes sensitivity of the sensors towards target gas A, and $\sum S_i$ is the sum of sensitivities for all the gases A, B, C and D, that is $\sum S_i = S_A + S_B + S_C + S_D$. Generally, the sensitivities are taken in percentage (% response) for the calculation of selectivity.

1.2.3. Stability

It is 'the ability of a sensor to maintain its reproducible performance of response through certain cycles or a period of time'. In order to evaluate the stability, repeated response of the sensor is measured for a particular concentration level, through the certain cycles of operation or periodically through a time zone.

In order to investigate the reproducibility of the gas sensor, *coefficient of variation* (CV) is calculated for a repeated response of the sensor towards a constant value of target gas concentration through a range of cycles. Mathematically 'it is the ratio of standard deviation to the mean of response magnitude'.

$$CV = \sigma/\mu \qquad\qquad (4)$$

1.2.4. Optimum working temperature

This is the value of temperature, at which the sensor possesses maximum sensitivity for a particular concentration level of the target gas. This is an important parameter regarding the performance of sensor, and it is the characteristic of material used, because every metal oxide works at particular operating temperature. Evaluation of power consumption is based on the working temperature. The higher the optimum working temperature, the higher is the power consumption.

1.2.5. Response and recovery speeds

These mean the response and recovery times of a gas sensor. Response time is defined is 'the time required to obtain 90% of the saturated value of resistance during its change upon exposure to certain target gas'. Recovery time is 'the time needed for attainment of 90% of the base-line value of resistance after the release of target gas'. Both response and recovery times determine the speed of sensor towards its cyclic operation.

1.2.6. Detection threshold or detection limit or limit of detection (LOD)

LOD is defined as 'the lowest concentration value of the target gas, which the sensor is able to detect at a particular value of operating temperature'. This is an important parameter esti-mating the lowest concentration extreme for a gas sensor, at which the resistance onsets changing.

1.2.7. Dynamic range

It is the range of target gas Concentrations, starting from detection limit to the highest value of limiting concentration, through which the sensor's response is measured. It evaluates the sensor's performance through an extended concentration zone.

1.2.8. Linearity

It is 'the deviation of the response calibration graph versus target gas concentration, from straight line'. It is obtained by linear fit of the response concentration curve for a metal oxide-based gas sensor, and the slope of linear fit is measured.

1.2.9. Life cycle

This is an important parameter which covers both the shelf-life as well as operating life. Operating life time is 'the period of time over which the sensor could be operated continuously'. The shelf-life is 'the maximum length of time, for which the sensor is stored after operation'.

2. Carbon nanotubes (CNTs)

2.1. Background and general classification

In 1991, during his experiment of electric arc discharge for fullerene production, Iijima [4] noticed that certain novel structures also produced which were named afterwards as carbon nanotubes. They are actually graphene sheets rolled specifically in the tube shape. Since that time, carbon nanotubes are the title of hardcore investigative research in different applications. Depending upon the range of diameters, carbon nanotubes may be classified in single-walled and multi-walled.

a. **Single-walled carbon nanotubes (SWCNTs)** consist of a bundle of string like which is a single-walled nanotube with diameter of the order of a nanometer (~1.4 nm) and inter-tube distance upto 0.3 nm approximately.

b. **Multi-walled carbon nanotubes (MWCNTs)** contain several graphene sheets rolled up in layers form, resulting in concentric tubes with increasing diameter. Due to significant Van der Wall forces, the MWCNTs are amassed together, giving typical diameter upto 10–20 nm, and their interlayer spacing upto ~0.34 nm.

More simply saying, carbon nanotubes can be considered as a macromolecule of carbon, very similar to a graphite sheet (which is used as your pencil lead) but wound in a cylindrical reel form (**Figure 1**). When graphite is coiled, the carbon arrangement takes as much strength as one hundred times of steel's and almost 2 mm long. Furthermore, these nanotubes exhibit flexibility, thermal stability and inertness chemically. They nanotubes are capable of either metallic or semi-conducting nature but it depends on the 'twirl' of the tube.
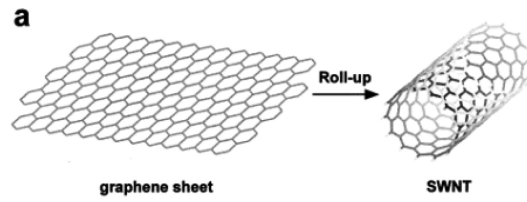
Figure 1. Roll of graphene into SWCNT [5].

Two important parameters for carbon nanotubes on which their electronic properties are supposed to be dependent are diameter and helicity (Chirality). Chirality is the degree of twist of the tube and is found by Chirality vector, denoted by C_h, given by [5]

$$C_h = n\mathbf{a} + m\mathbf{b} \tag{5}$$

where $\mathbf{a}$ and $\mathbf{b}$ are unit vectors of the hexagonal lattice. n and m are integers which denote chiral vector as (n,m) expression (**Figure 2**). Axis of nanotubes and chiral vector both are orthogonal to each other. Using the values of n and m, diameter and Chiral angle (Chirality) are calculated as following:

$$d_t = C_h / \pi \tag{6}$$

and
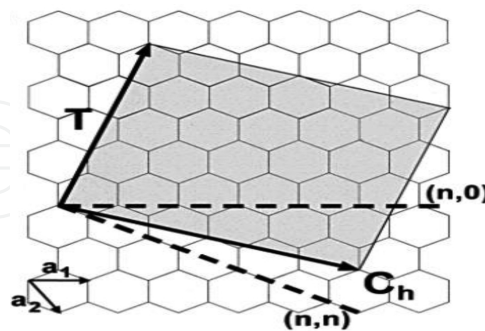
$$cos\theta = \frac{2n+m}{2\sqrt{n^2+m^2+nm}} \tag{7}$$

Figure 2. Schematic representation of a 2D graphene sheet illustrating lattice vectors a1 and a2, and the roll-up vector na1 + ma2 [5].

Tubes are classified into zigzag and armchair tubes, according to the different values of θ which can take the values from 0° to 30°.

a.   For θ = 0°, m = 0, we have (n, 0) type tubes, which are called zigzag tubes.

b.   For $\theta = 30°$, m = n, we have (n, n) type tubes, which are called armchair tubes.

Metallic or semiconducting nature of the tubes can also be determined by (n, m) indices. Metallic conductivity comes for the three cases.

a.   Armchair tubes with indices (n, n).

b.   Zigzag tubes with indices (n, 0) in which n and n–m are the multiples of 3.

All other tubes with arbitrary (n, m) values are semiconducting. For a random distribution of nanotubes, statistical analysis predicts that approximately ⅓ are metallic and ⅔ are semiconducting [6].

2.2. Electronic transport

Discovery of carbon nanotubes and their studies thereafter have opened new frontiers of science and industries. Unique geometrical features of carbon nanotubes are convincing towards facing of certain quantum mechanical problems which might be helpful in low-dimensional physics as well. In this section, we will study certain specific aspects of the electron transport in both single-walled and multi-walled CNTs which cannot be taken into account in case of mesoscopic physics generally. A new phenomena of Aharonov-Bohm will be described Which has recently been investigated in CNTs-based field effect transistor devices. The role of chemical doping/composite in case of intrinsic transport and interfacial effects will also be given a touch. Such interfacial effects have vital significance in sensing technology.

It has been reported that electronic transport properties of the nanotubes are connected with their electronic band structures which consist of multiple one-dimensional sub-bands sliced from the Dirac sliced from the Dirac dispersion cone of graphene.

2.3. Gas sensors based on CNTs

Conductometric gas sensors work on the principle of change in resistance due to the interaction with target gas molecules. It has been reported that gas sensors based on semiconducting carbon nanotube offer high sensitivity, quicker response, and better portability towards certain target gases (such as NO_2 and NH_3) as compared to conventional thin-film gas sensors [7].

2.3.1. History and working principle

After the discovery of CNTs in 1991, just like other devices, a gigantic research run was embarked on to investigate their use in gas-sensing devices as well. Their synthesis, possessions (such as electronic, mechanical and thermal) and applications in different areas are being studied deeply. Both calculative and experimental works are also being conducted for their better understanding. Researchers all over the world are in search of their performance as gas sensors such as NASA's researchers are doing for the identification of atmospheric components of various planets. When they are exposed to certain gases, variation in their different properties is detected by various methods.

2.3.2. Device fabrication techniques based on CNTs

Carbon nanotubes are grown through arc-discharge, laser ablation and chemical vapour deposition (CVD) methods [8]. In order to fabricate CNTs-based gas sensor device, three techniques are generally applied [9].

2.3.2.1. Casting technique

One way is to caste CNTs on interdigitated electrodes (IDEs). In this method, the electrodes are fabricated by photolithography technique and evaporation of Ti and Au on silicon oxide. As-grown SWCNTs are purified with acid first and then by air oxidation before they could be integrated with the IDEs [10]. The major advantage of this method is that purified nanotubes are obtained so that the impact of impurities can be minimized. These purified nanotubes are then dispersed in the dimethylformamide (DMF) and drop-deposited onto the electrode area. Finally, the DMF is evaporated such that a network of nanotubes is subsequently obtained. This device fabrication technique was developed firstly by Li et al. for SWCNTs-based gas sensor device.

2.3.2.2. Screen printing

This is another simple technique which is widely used for the fabrication of gas sensor device. In this method, CNTs paste is mixed with organic binders (terpineol, ethyl cellulose) and glass frits are printed on electrodes coated glass or tube. The organic binders are removed by evaporation through annealing in N_2 atmosphere. Lee at al. first used this technique to fabricate MWCNTs-based gas sensor for NO_2 gas detection.

2.3.2.3. Dielectrophoresis (DEP)

It is another technique which is used for the fabrication of CNTs-based sensors. It is the electrokinetic motion of dielectrically polarized materials in non-uniform electric fields which is used to manipulate CNTs for separation, orientation and positioning. This technique can establish a good electrical contact between CNTs and the electrodes. Suspension of highly purified CNTs in ethanol is ultrasonicated for some time. A glass substrate is patterned with castle-wall-typed interdigitated microelectrode so that high and low are formed periodically. This electrode is surrounded by a silicon rubber spacer in the form of a sealed chamber, and the CNTs suspension is continuously injected by a peristaltic pump. An AC voltage is applied for the DEP trapping of CNTs on the microelectrode for a definite period of time. Finally, the DEP process is stopped and ethanol is evaporated at room temperature. Suehiro et al. applied this technique for the MWCNTs-based gas sensor devices to detect various target gas vapours such as NH_3, NO_2, SO_2 and HF.

2.3.3. Gas adsorption on carbon nanotubes; parametric analysis

Using first-principles calculations by density function theory, adsorption of various target gases on CNTs has been studied by Peng and Cho as well as Zhao. Such an adsorption is

characterized by three parameters, that is tube-molecule distance (d), adsorption energy (E_a) and charge transfer (Q) [11].

2.3.3.1. Tube–molecule distance (d)

It is defined as the nearest distance between atoms on the molecule and the nanotube for T site (top of a carbon atom), or the distance between the centre of the gas molecule and the centre of the carbon hexagon (carbon–carbon bond) for the B site (top of centre of the C–C bond).

2.3.3.2. Adsorption energy (E_a)

It is defined as the total energy gained by molecule adsorption at equilibrium distance. Mathematically,

$$E_a = E_{total(Tube+gas\ molecule)} - E_{(tube)} + E_{(Gas\ molecule)} \tag{8}$$

When $E_a < 0$, the reaction is exothermic and spontaneous, that is high value of adsorption energy releases more energy during the reaction. However, for $E_a > 0$, it is relatively hard to continue the reaction because of the amount of energy required.

2.3.3.3. Charge transfer (Q)

It denotes the total Mulliken charge number on the molecules, If Q is positive then charge transfers from molecule to tube. It has been shown computationally that large charge transfer changes the resistance (or conductance) of the tubes. Such changes are recorded by voltage variation which could be related to the gate capacitance of the device. Mathematically,

$$\Delta Q = C_g \Delta V_g = \delta\theta\left(\pi dl \middle/ \sigma\right) \tag{9}$$

Here, C_g is the nanotube capacitance, ΔV_g is the change in voltage recorded during experiment. 'd' is diameter, and 'l' is the length the CNT, σ is the molecules cross-sectional area, and $\delta\theta$ is the coverage of the molecules over the CNT's surface.

2.3.4. Electronic transport dependency over molecular adsorption of target gases

We know that generally the electronic properties of CNTs are determined by their chirality and diameter [12]. However, experimental evidences demonstrate that the electronic properties are also very sensitive to the gaseous environment around CNTs, particularly when they are exposed to oxygen. Such a variation in CNTs electronic properties are attributed towards the charge transfer between CNT and target gas molecules where the molecules act as electrons' donors or acceptors. In case of no charge transfer, the resistance variation is mainly due to the variation in carriers' free lifetimes and mobility. It has therefore been concluded that the electrical response of SWNTs bundle to various target gases can either be due to the

change of fermi level due to the charge transferring or by the additional scattering channel for conduction electrons in the walls of the CNT. Mathematically, this can be understood by following equation [13]:

$$S = S_o + \left(\frac{\rho_a}{\rho_o} \right) (S_a - S_o) \qquad (10)$$

where S_o and S_a denote the thermopower contributed from the host resistivity ϱ_o, and the impurity resistivity ϱ_a associated with target gas adsorbed, respectively. This equation is also known as the Nordheim-Gorter (N-G) relation [14]. Its shows mathematically whether the gas molecules are physisorbed or chemisorbed.

2.4. Mechanism-based design classification of CNTs-based gas sensors

As we have mentioned earlier that the electronic properties of CNTs are very sensitive to the exposed environment due to the gas molecule adsorption. Physical quantities such as thermopower, resistance and density of states of single SWNT or SWNT bundles vary on exposing them to certain gases. Sensors with resistance variation on exposure to the target gases are generally termed as conductometric gas sensors. Due to the easy manufacture and portability, conductometric sensors are the most commonly used architecture in the design of CNTs gas sensors. Such sensors have further following subclasses on the basis of architecture.

2.4.1. Semiconducting CNTs FET gas sensors

We know that CNTs can be semiconducting as well as metallic. If we connect a semiconducting CNT in between two metal both sides, it forms a metal/semiconducting/metal-type device which behaves as p-type transistor. Therefore, the resistance variation of CNTs to the target gas adsorption can be recorded with field emit transistors (FETs). Compared with SWCNTs, the mechanism of MWCNTs' response to gas adsorption is more complicated due to the multilayer tube structure. However, they also show high sensitivity to specific gases experimentally [15, 16].

2.4.2. CNTs-based two terminal gas sensors

The change in resistance of CNTs after exposing them to gaseous atmosphere can also be detected by resistors with two terminals connected with dc voltage. In these kinds of gas sensors, the interdigitated electrodes are applied to provide larger sensing areas and sufficient contacts between the electrodes and the coated CNTs [17].

2.4.3. Carbon nanotubes enhanced ionization chamber for gas sensing

The major drawback of the chemical gas sensors is that gas molecules with low adsorption energy are hardly detectable with them. Therefore, another type of sensors called ionization gas sensor are applied. Such sensors are based on the finger printing ionization characteristics

of the target gases. Their working is based on the gaseous molecules' ionization due to their collisions with the accelerated electrons. Practically, there is no adsorption and chemical interaction between the sensing device and target gas molecules. Hence, adsorption energy and charge transfer with the sensing material are not the desired parameters in such sensors. Detection of inert gases or gas mixtures can easily be achieved by ionization chamber, which in turn delivers better selectivity. However, such sensors are bulky in architectures, with considerable high power consumption and breakdown voltage, which are industrially functional drawbacks. Carbon nanotubes can lead to the large field enhancement factor, thereby increasing the electric field around the tips reasonably and produce corona discharge at very low voltages [18]. This has shown importance in ionization gas sensors [19–27]. Besides this, CNTs are good emitter sources of electrons because they have very sharp tip curvature and low electron escaping work function.

Another important factor that dominates the ionization characteristic is the inter-electrodes distance. According to Paschen's curve, in order to induce the breakdown phenomenon, a certain gap distance is required, and a decrease in the breakdown voltage occurs with reducing the inter-electrodes distance.

Integrated dielectric barrier discharge (DBD) mechanism is a general technique used to fabricate the novel ionization gas sensor with short-gas spacing, CNTs and DBD coating to realize low power consumption and breakdown voltage. It has been shown that the DBD layer effectively lowers the breakdown voltage and improves the reproducibility of the device [25].

2.4.4. CNTs-based gas-sensing capacitor

These sensors are based on the randomly aligned carbon nanotubes and are used for humidity sensing. The structure of such a sensor is shown in **Figure 3**.
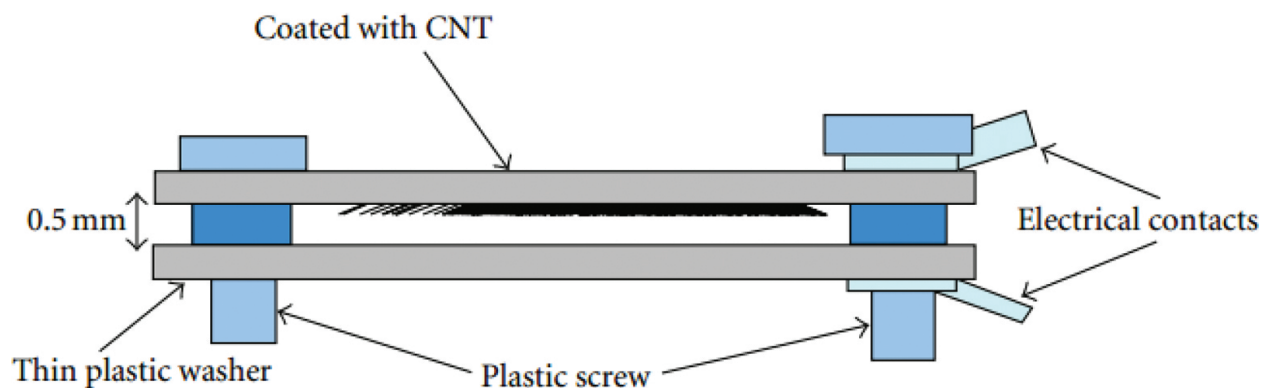

Figure 3. Parallel plate capacitive as a humidity sensor with MWNTs deposited on one plate.

Capillary condensation is responsible for the increase in the capacitance under high relative humidity. Such a condensation effect is induced by the nanopores and interstitial gaps in the random aligned CNTs structure.

2.4.5. CNTs-based resonator sensor

The working principle of these sensors is based on the change of the electrical properties (resonant frequency) of the sensing materials in the gaseous exposure. Circular disk resonators with SWCNTs coated on top of the disk have been used as resonator sensor. Resonant frequency is given by following relation;

$$f_o = \frac{1.841c}{2\pi a \sqrt{\epsilon_r}} \qquad (11)$$

where 'f_o is the resonant frequency, c is the light's speed in vacuum, a is the radius of the disk, and ϵ_r denotes the relative dielectric constant of the substrate'. When the CNTs-based resonator sensor is exposed to certain target gas vapours, the alternation of the dielectric constant of the circular disk with CNTs on top induces the resonant frequency shift.

2.5. Pre-functionalization of CNTs, a recent strategy

Although as-prepared/as-obtained carbon nanotubes can be used to fabricate gas sensors of any type as discussed in the last section; however, their sidewall functionalization improves their performance which opens new doors for their applications in many areas [28–30].We have studied that the electronic sensitivity of CNTs to various target gases is highly limited by the binding energy and charge transfers of the molecules with the CNTs wall. When they are functionalized, active bonds appear on the side walls of CNTs which would indeed enhance their sensing capability towards wide range of gaseous vapours [31].

It has been investigated the resistance response of chemically functionalized MWNTs (f-CNTs) to alcohol vapours with ultralow power consumption [32]. For the fabrication of the sensor, purified MWNTs are chemically functionalized in acidic media. To do so, pure CNTs (commonly, MWCNTs) are sonicated in a mixture acids. It is believed that after chemical functionalization, the polar COOH groups are attached onto the nanotubes surface. The sensors will therefore give stronger responses to the alcohol. This is due to the fact that their absorption efficiency with these volatile organic molecules will be increased due to the dipole–dipole interactions (mainly hydrogen bonding) between the COOH and the polar organic molecules. Although CNTs have been proven as a good material for sensor, yet, the pure CNTs have almost zero response to H_2 because they have very week binding energy [33]. However, when they are functionalized with materials such as Pt or Pd, CNTs may be very sensitive to hydrogen as well [34, 35]. Basic mechanism for such improvement is that the hydrogen molecules dissociate into atomic hydrogen on Pt/Pd surfaces and form PtH_2/PdH_2, which lowers the work function of Pt/Pd and causes the electron transfer from Pt/Pd to MWNTs [36–38].

The question is that how can we functionalize CNTs efficiently? Several methods are used to obtain f-CNTs. Reflux of CNTs in acidic media (HNO_3 or HCl or H_2SO_4 or their mixtures) is very common nowadays. Such a chemical acidification activates the surface bonding of CNTs which would then readily interact with the target gas vapours as discussed earlier.

2.6. Literature survey regarding CNTs-based gas sensors

Since its discovery in 1991, carbon nanotubes have been the core research topic in various areas of applications. Sufficient work has been done by others; however, there is still certain gap in some circumstances, and therefore, researchers are still in an extensive run to optimize the properties of carbon nanotubes for different industries such as cathodes for supercapacitors, batteries, and gas sensors.

In order to obtain gas sensors based on carbon nanotubes, the first step is to fabricate a good sensor device which could execute certain functional and architectural advantages such as easy in manufacturing, portable, economical, capable to be utilized in all weathers with minimum seasonal effects, consume low power during operation, high sensitive as well as selective and reproducible as well. Various methods are used to fabricate a good sensor device as described in previous sections. Earlier, several efforts in this regard have been reported in literature. Li et al. designed a conductive gas sensor by casting SWCNTs on the interdigitated electrodes (IDEs) [39]. Such a device is shown in **Figure 4**.

Lee et al. used screen-printing technique to fabricate a simple gas sensor device based on CNTs. CNT paste was mixed with MWNTs, terpineol, ethyl cellulose, and glass frits onto electrode-coated glass as the gas-sensing element for NO_2 detection. The organic binder was removed by annealing in N_2 ambient [40].

Dielectrophoresis (DEP) method has been used by Suehiro et al. [41]. During fabrication, the CNTs with high purity were ultrasonicated in ethanol for 60 min. The system to fabricate the CNTs-based gas sensor is schematically depicted in **Figure 5**.
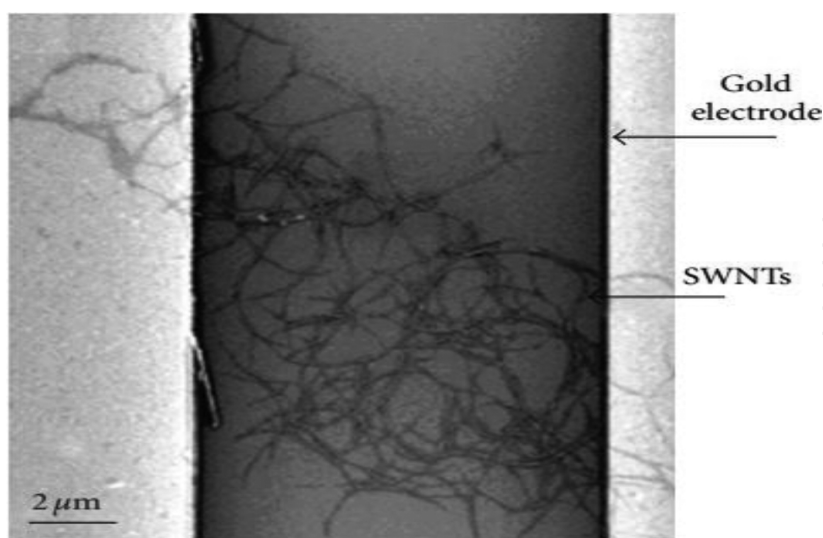

Figure 4. SEM image of SWCNTs across two gold electrodes [39].

Such DEP-fabricated CNTs gas sensors successfully detected various target gas vapours such as ammonia, nitrogen dioxide, sulphur dioxide and hydrogen fluoride.
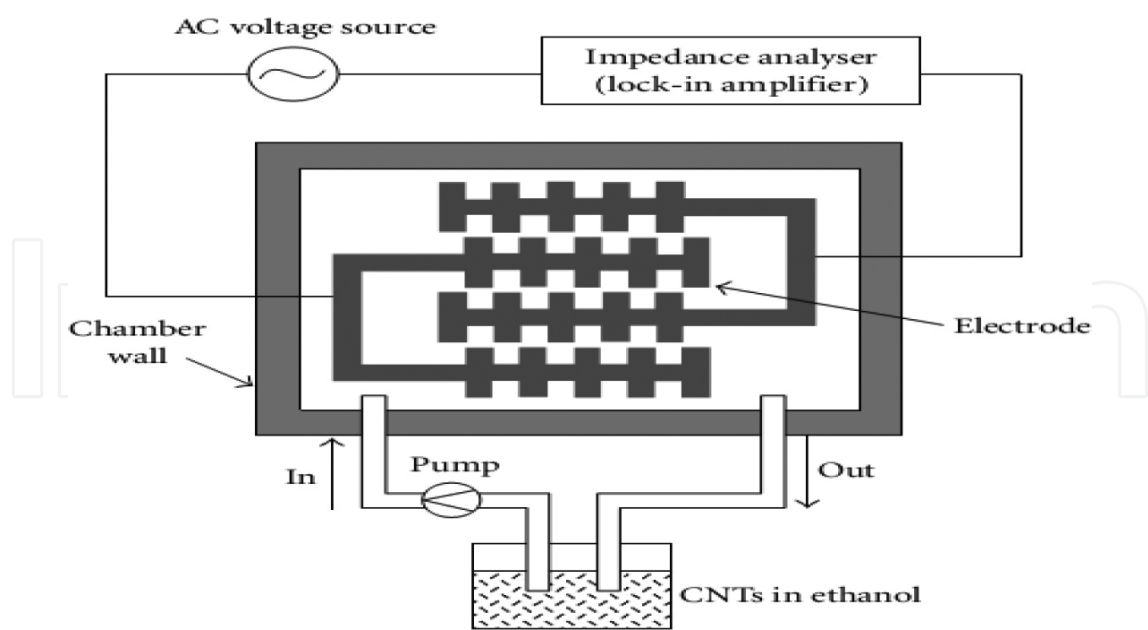
Figure 5. Schematic diagram of the experimental set up for MWCNTs-based gas sensor device by DEP method.

A three terminal gas sensor device based on vertically aligned CNTs for N_2 gas has been fabricated successfully by Huang et al. [42]. The CNTs were grown by thermal CVD on a silicon substrate at 700°C. Substrate was pre-heated and then cooled down at room temperature in N_2 ambient. A 30-nm-thick Fe layer was sputtered on the substrate as catalyst, and C_2H_2 was used as the carbon source. The as-grown CNTs mat is shown in **Figure 6**.
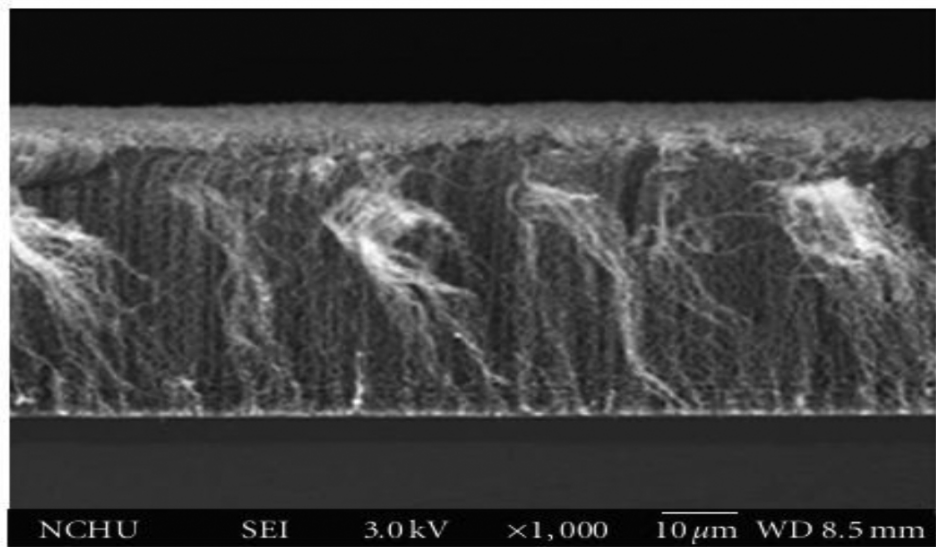

Figure 6. Vertically aligned CNTs mat (cross-sectional image) [45].

An ammonia sensor based on laterally aligned MWCNTs has been fabricated by Jang et al. [43]. A substrate of N-type heavily doped Silicon wafer with SiO_2 layer on top was used, and the

Nb electrodes were deposited and patterned on it. Such a gas sensor device with detailed steps of fabrication is depicted in **Figure 7**.
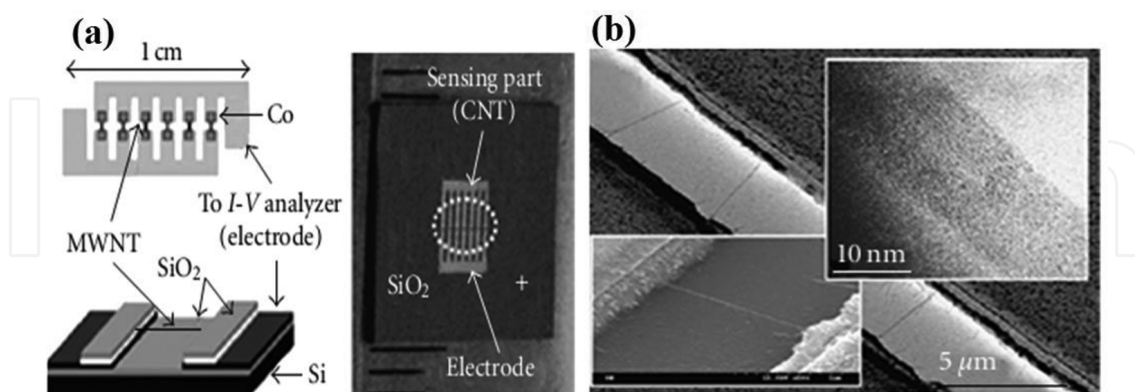

Figure 7. (a) Ammonia chemical sensor based on laterally aligned MWCNTs, (b) aligned CNTs on SiO_2 surface. TEM image of laterally grown CNTs (inset) [43].

NH_3OH and HCl sensor devices based on self-aligned and self-welded MWCNTs were prepared successfully between pre-patterned electrodes by Tabib-Azar and Xie, through a low-pressure CVD (LPCVD) method [44].

In order to study the adsorption of target gas molecules over the CNTs surface and the resultant-induced effects, Peng and Cho applied first-principles calculations using density functional theory and investigated the adsorption of NO_2 gas on SWCNTs surface and resultant changes in various parameters [11]. Binding configuration of NO_2 on semiconducting (10, 0) SWCNTs surface was obtained which showed that the NO_2 gas molecule of such a configuration was found to bind with SWNT with adsorption energy of 0.3 eV. It was also found that the NO_2 molecule has high diffusion kinetics on nanotubes surfaces. Electron density analysis was also carried out which reveals that charge transfer is induced from C atom to the NO_2 gas molecule, thus leading to p-type (hole) doping of these (10, 0) SWCNTs.

Such DFT calculations were also performed by Zhao et al. with the adsorption of molecules of various gases such as NO_2, O_2, NH_3, N_2, CO_2, CH_4, H_2O, H_2 and Ar, on both individual SWCNT and SWCNT bundles [48]. In case of individual SWNT, the data calculated for equilibrium tube–molecule distance, adsorption energy and charge transfer towards various target gas molecules on (10, 0), (17, 0) and (5, 5). SWNTs is shown in **Table 1**.

Results in **Table 1** reveal that the gaseous molecules (except for NO_2 and O_2) are charge donors with minute charge transfer (0.01–0.035 e) and weak binding energies (≤0.2 eV). These gas molecules can be identified as physisorbed. For the gases O_2 and NO_2, it is shown that both of them are charge acceptors with large values charge transfer and adsorption energies. These results are in good consistency with the experimental data [46, 47]. Furthermore, no clear dependence of adsorption on the tube size and chirality was proved.

	NO$_2$	O$_2$	H$_2$O	NH$_3$	CH$_4$	CO$_2$	H$_2$	N$_2$	Ar
(10, 0) SWNT									
d (Å)	1.93	2.32	2.69	2.99	3.17	3.20	2.81	3.23	3.32
E_a (meV)	797	509	143	149	190	97	113	164	57
Q (e)	−0.061	−0.128	0.035	0.031	0.027	0.016	0.014	0.008	0.01
Site	T	B	T	T	C	C	C	C	C
(5, 5) SWNT									
d (Å)	2.16	2.46	2.68	2.99	3.33	3.54	3.19	3.23	3.58
E_a (meV)	427	306	128	162	122	109	84	123	82
Q (e)	−0.071	−0.142	−0.033	0.033	0.022	0.014	0.016	0.011	0.011
Site	T	B	T	T	C	C	C	C	C
(17, 0) SWNT									
d (Å)	2.07	2.50	2.69	3.00	3.19	3.23	2.55	3.13	3.34
E_a (meV)	687	487	127	133	72	89	49	157	82
Q (e)	−0.089	−0.096	0.033	0.027	0.025	0.015	0.012	0.006	0.01
Site	T	B	T	T	C	C	C	C	C

The optimal adsorption sites: T (top of a carbon atom), B (top of the centre of the C–C bond), C (top of the centre of carbon hexagon).

Table 1. Data for equilibrium tube–molecule distance (d), adsorption energy (E_a) and charge transfer (Q) of various molecules on (10, 0), (17, 0) and (5, 5) individual SWNTs [45].

In case of SWCNTs bundle, following four distinct sites are specified for the adsorption of gas molecules [48, 13]:

a. External surface of the nanotubes bundle,

b. The groove formed at the contact between adjacent tubes on the outside of the bundle,

c. The interior pore of individual tubes,

d. Interstitial channel formed between three adjacent tubes within the bundle.

Adsorption of the target gas on these sites is decided by two parameters such as

a. The binding energy of the target gas molecules,

b. Availability of the sites on CNT surface.

Reason for such determination is that out of above-mentioned four sites, some sites may not adsorb the gas molecules due to mismatch of the dimension of molecule and the site diameter. The c-site (interior pore of the tube) can be accessed by molecules only in following cases [49];

a. SWCNT is uncapped,

b.   SWCNT has defects on the tube walls.

Binding energies and contribution of specific surface area for the adsorption of H_2 gas molecules as calculated by Williams and Eklund [47], are shown in **Figure 8**.
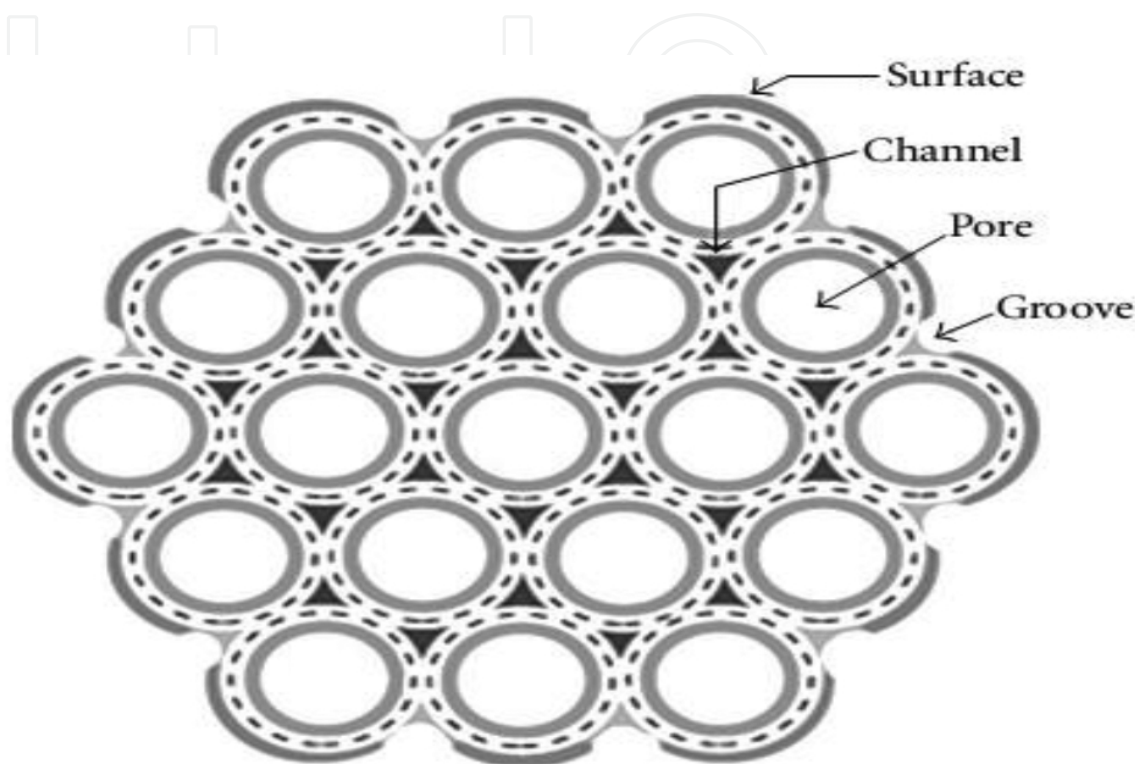

Figure 8. Schematic structure of SWNT bundle with available sites for gas adsorption [47].

The binding energy data in **Table 2** shows that in the order of increasing, following order holds good:

$$E_{B(channels)} > E_{B(grooves)} > E_{B(pores)} > E_{B(surface)},$$ (12)

S. no.	Site	Binding energy (eV)	Specific surface area (m²/g)
1.	Channel	0.119	45
2.	Grooves	0.089	22
3.	Pores	0.062	783
4.	Surface	0.049	483

Table 2. Binding energies and specific surface areas of specified sites.

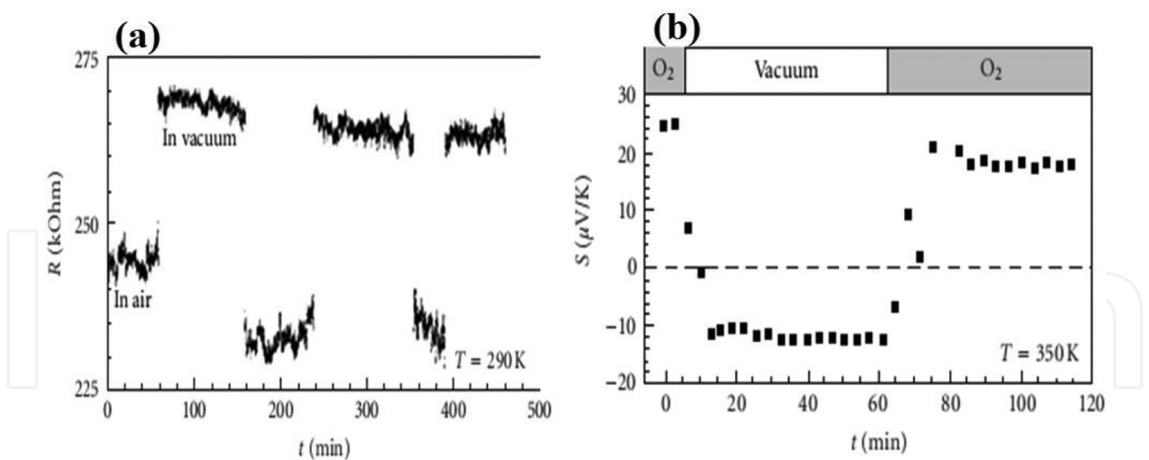Specific surface areas for the pores and surface have larger values.

Figure 9. (a) Sensitivity of the electrical resistance 'R' of SWNT films to the gas exposure, and (b) sensitivity to environmental conditions of thermoelectric power 'S' for SWNTs. In vacuum, S is n-type, whereas in oxygen exposure, S is p-type, with a larger magnitude [46].

Several other parameters, such as electrical resistance, thermoelectric power and local density of states, for CNTs exposed to target gas molecules have also been measured. The work done by Collins et al. [46] in this regards sounds better. Using transport measurement and scanning tunnelling spectroscopy, they measurement these parameters and found that all these three parameters change reversibly even when SWCNTs are exposed to small concentration of oxygen (**Figure 9**).

Likewise, effect of degassing on these parameters for SWCNTs was studied by Sumanasekera et al. at 500 K [49] and it was found that thermoelectric power decrease slowly from 54 μV/K and reversibly approach to a constant value of -44 μV/K (**Figure 10**). Spin–lattice relaxation of all the SWCNTs was also studied using nuclear magnetic resonance (NMR) for which a dramatic increase was observed in the oxygen exposure.
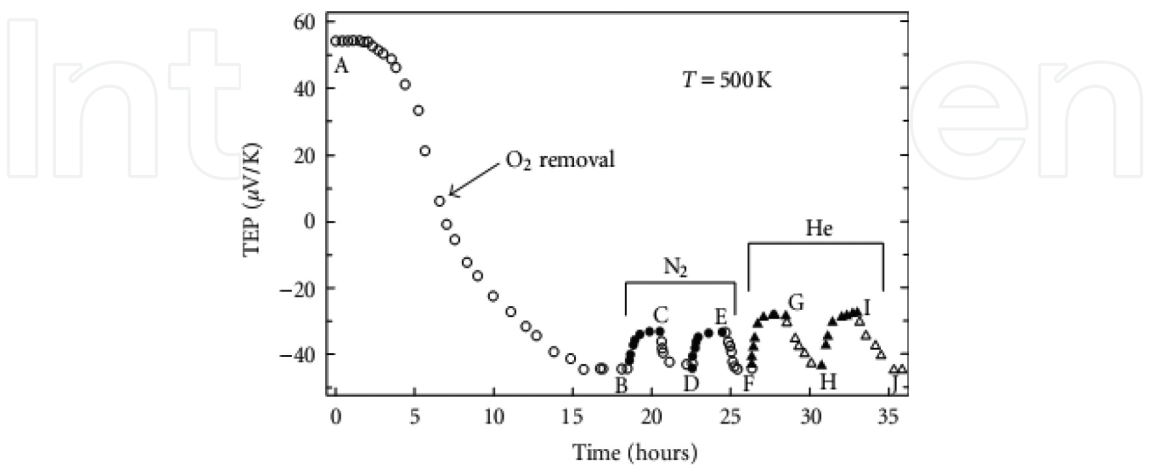

Figure 10. Thermoelectric power 'S' versus time for a mat of SWNTs at T = 500 K initially saturated with air at ambient conditions.

Besides oxygen, the effect of alcohol (methanol, ethanol, isopropanol and butanol), ammonia and water molecules on the electrical transport of SWNT bundles have also been studied and it was found that both thermoelectric power and resistivity (resistance) varies strongly with the alcoholic exposure [40]. All the alcoholic molecules were found to be physisorbed on the tube wall as indicated by the Nordheim-Gorter N-G equation plot (**Figure 11**).

A linear N–G plot indicates physisorption of the gaseous molecules. Significant effect of water vapours over the resistance was observed as well; however, it did not alter the thermoelectric power. Curved-type N–G plot for the ammonia and water shows the chemisorption of the adsorbed molecules.
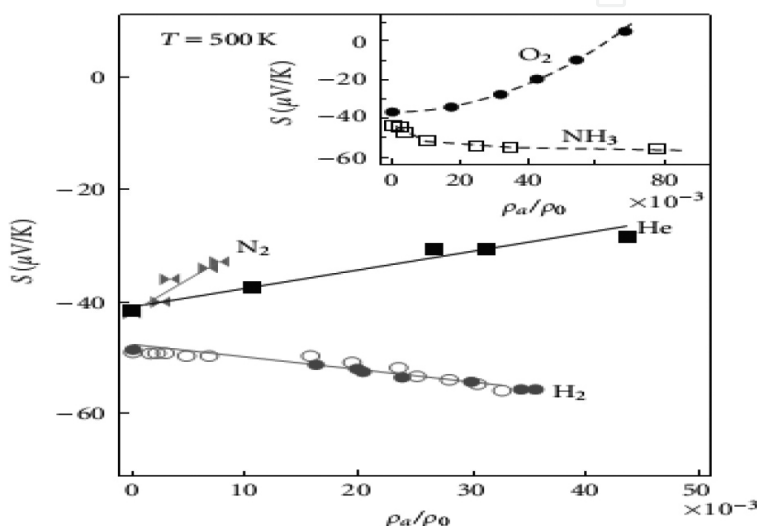

Figure 11. N–G plots (S versus ϱ) showing the effect of gas adsorption on the electrical properties of the SWCNTs bundle [49].

As far as the design and sensing properties of the CNTs-based gas sensors on the basis of sensing mechanism is concerned, several researchers took the charge in this regard. The efforts made by Kong et al. [34] are of vital significance, who fabricated a semiconducting SWCNT FET from a single SWNT for chemical sensing. The single SWCNT was grown on SiO_2/Si substrate with patterned catalyst islands, through a controlled CVD in which the polysilicon on the back side acted as gate of the transistor. Room-temperature plot of conductance versus time was recorded towards NO_2 and NH_3 (**Figure 12**). It was observed that exposing the device to 200 ppm of NO_2, a sharp increase in the conductance (about three orders of magnitude) is obtained (**Figure 12a**). The sensitivity magnitude of 100–1000 with a quicker response time of 2–10 s response indicated that the device is significantly sensitive towards NO_2 gas molecules. In 1% NH_3 exposure, a dramatic decrease in conductance along with sensitivity of 10–100 was observed which further reveals the sensitivity of the SWCNT-based FET gas sensor device towards ammonia as well (**Figure 12b**).

Another contribution by Huang et al. [41] has been reported who fabricated the gas sensor device based on the vertically aligned MWCNTs bundle with FET structure through thermal CVD and investigated change of resistance (and hence sensitivity) towards the nitrogen (N_2)

gas. P-type semiconducting behaviour was observed and resistance increased with exposure to N_2. The increasing resistance showed an electron donor role of the CNTs and decreasing the concentration of conducting holes on CNTs. The sensor showed relative fast response and the resistance returned back to its initial value in vacuum, which indicated the physisorption of the N_2 molecules.
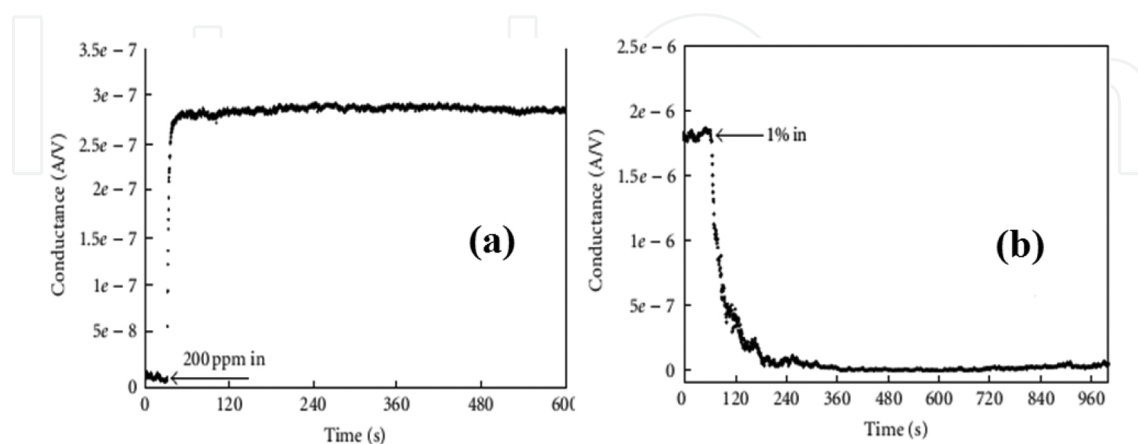

Figure 12. Conductance change of the single SWCNT-based FET sensor when exposed to (a) NO_2 and (b) NH_3 gases [34].

Gas-sensing performance of the sensor based on chemically functionalized MWCNTs has been investigated by Sin et al. [31], and he found that the sensor responded to alcohol vapours at low working temperature (with very low power consumption). The sensor also responded linearly to the alcohol vapour in the concentration range of 1–21 ppm with good selectivity to oxygen, water and alcoholic vapours. These functionalized MWCNTs deliver 0.9–9.6% higher sensitivity magnitude as compared with the un-functionalized MWCNTs.

All these literature reports reveal the feasible sensing nature of carbon nanotubes (both SWCNTs and MWCNTs) and describe their significance as sensing material. Just like the use of CNTs in other applications, a competitive research run in the field of chemical (gas) sensors has been in practice since its first discovery. However, in order to improve the stability and sensitivity effects of CNTs, recently preparation of their composites with the external materials (conducting polymers, etc.) is being intensely focused by the research community.

3. CNTs/polymer nanocomposites

3.1. Review and significance

Polymer is basically a large molecule (macromolecule), which is composed of many repeated units. Such a repeated structure delivers polymers following unique properties;

a.   Low density

b.   Reasonable strength

c. Good flexibility

d. Easily processable

Polymers occur in two types, that is natural and synthetic. Due to a wide range of properties, both types of polymers exhibit play vital and significant role in industries.

In spite of their numerous properties, the limited mechanical properties of polymers have restricted their use in many engineering applications. Therefore, research community is in continuous run to explore new and novel polymeric materials with improved properties. The first step in this regard was the amalgamation of different polymers to obtain new materials with enhanced properties. However, this leads to only a marginal improvement in properties and their industrial use still remained a question. Then, the strategy of using different organic and inorganic fillers was applied to improve the strength and stiffness of the polymers. The use of long fibres as fillers with the thermosetting polymers enhanced the mechanical properties. However, the processing of polymers with such kinds of fillers is extremely difficult which lacks its commercialization. Therefore, small particles/fibres reinforced composites were applied as a next strategy. Different metals' particles, carbon black and silica, etc., were used as these fillers. Advancement in mechanical properties to a desired range was obtained with the loading of these fillers to a higher level, and consequently this increased cost and they were also not easily processable. Therefore, further tactics in this regard were applied which include the loading of nanofillers at low levels and these nanofiller reinforced polymer matrix are known as polymer nanocomposites.

3.2. Polymer nanocomposite materials

As we have described earlier, those polymer nanocomposites are a new class of advanced composite materials, which have been receiving much attention on research and commercial levels. The dimensions of nanofillers incorporated in these materials are only up to a few nanometers (about 1/10,000 of human hair), due to which they offers ultra-large interfacial specific area between the nano-element and polymer matrix. Resultantly, the polymer nanocomposites display significant enhancement in toughness, thermal stability, etc., without compromising on their other properties such as stiffness or optical clarity.

3.3. Why CNTs–polymer nanocomposites

As compared with the other nanofillers, carbon nanotubes (CNTs) have been shown as the most promising nanofiller materials for polymer composites and this credit goes to their remarkable mechanical and electrical properties [50]. CNTs have been under-investigation as a nanofiller for polymer nanocomposites since the day of its first discovery. In order to take the advantages of CNTs and their extra ordinary properties in everyday life, CNT/polymer nanocomposites were explored and investigated for many purposes and these research efforts have led them favourable in many fields, which include energy sector, defence equipments, automobile industries sports, supercapacitors and gas sensors. These multi-dimensional applications of CNT/polymer nanocomposites are actually based on their flexible processing methods, ultra-high strength, light in weight and good durability. Moreover, the high value

of electrical conductivity, CNT/polymer nanocomposites are usable as electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding materials. However, the feasibility of CNTs to fabricate their polymer nanocomposite materials depends mainly on their homogeneous dispersion throughout the polymer matrix without losing their integrity.

In the following sections, we will discuss different fabrication methods of polymer nanocomposites and their numerous properties briefly. Then exploration of their gas-sensing properties will be described in detail. Finally, we will sort out the gas-sensing mechanisms for these nanocomposite materials in the light of literature report.

3.3.1. Preparation strategies

We have learnt that CNTs have strong tendency of aggregation due to their large surface area which provide them the ability to be bonded with the polymer matrices. Such a combination lasts until and unless large forces are applied. Such large and un-bearable forces mainly come from the vigorous mixing of the polymer which can damage the CNTs structure as well. Therefore, during their processing of CNT/polymer nanocomposites, the biggest issue is the proper dispersion of individual CNTs in the polymer matrices so that the advantages of CNTs' prominence be fully realized. Pre-functionalization of CNTs chemically has helped is their dispersion to some extent, but then the main issue is their long term stability. Following methods are in use to process the CNT/polymer nanocomposites in recent research.

a. Solution blending

b. Melt mixing

c. In situ polymerization

3.3.1.1. Solution processing (solution blending)

This is most common method used to prepare CNT/polymer nanocomposites. In this method, both CNTs and polymer are mixed in a suitable solvent. The main advantage of this method is that CNTs are mixed rigorously by dispersion. Generally, it consists of three steps such as

Dispersion of nanotubes in a suitable solvent by magnetic stirring, ultrasonication or refluxing. However, sonication for longer time can shorten the nanotubes which reduce the aspect ratio of CNTs and are unfavourable to the properties of nanocomposites.

Mixing of CNT dispersion with the polymer (either at room temperature or elevated temperature),

Final yield of nanocomposite by precipitation or casting of a film.

It is notable that both organic and aqueous medium are used to produce CNT/polymer nanocomposites [51]. To minimize the shortening of nanotubes by sonication, suitable surfactants are used to get better dispersion. Sodium dodecylbenzene sulfonate, K-30, etc., are common surfactants used for this purpose [52].

In spite of the advantages of the solution-processing technique for the better nanotube dispersion, it is industrially less favourable due to its less yield.

3.3.1.2. Melt blending

In order to obtain large scale production on industrial level, melt processing is a preferred option because it is relatively economical and simple to process. Generally, this method consists of two steps;

Melting of the polymer pellets to form a viscous liquid,

Apply high shear stress to disperse the CNTs in this viscous liquid.

This method has been used successfully to prepare MWCNT/polycarbonate, [50] MWCNT/ nylon-6, [51] SWCNT/polypropylene [52] and SWCNT/polyimide [53] nanocomposites.

Although this is a simple technique, the major problem with it is that the application of high shear force and high temperature for melting purpose may weaken the properties of nano-composites as well as the CNT fragmentation. Therefore, there must be an optimum value of the shear stress and temperature to get the required dispersion. To overcome these issues, several modifications have been introduced in melt blending, for example, combining the solution-melt blending techniques and then applying several cycles of melt processing [54], introduction of polymer-coated MWCNT (instead of pure MWCNT) into the melted polymer to promote compatibilization [55].

3.3.1.3. In situ polymerization

This technique is common nowadays, particularly to prepare of polymer grafted nanotubes where polymers are insoluble and thermally unstable. The main advantage of this method is that it enables grafting of polymer macromolecules onto the walls of CNTs. Besides this, it enhances the miscibility of CNTs with almost each polymer matrix. Depending on the desired molecular weight and molecular weight distribution of polymers, several types of polymeri-zations (such as chain transfer, radical, anionic and ring-opening metathesis) can be used for in situ polymerization processing. For the first time, this was applied for the preparation of PMMA/MWCNT nanocomposites [56–58]. Later on, the preparation of hydroxyl functional-ized MWCNTs/acrylic acid-grafted PTT nanocomposites [59], SWCNT-reinforced polyimide nanocomposites [60], etc., have been reported by using this technique.

3.3.2. Inter-constituents' interaction in the CNT/polymer nanocomposite

We have studied that introduction of CNTs to the polymer matrices upgrades their different properties including electrical, mechanical, morphology and thermal properties, of the resultant nanocomposites. Best performance of the CNTs/polymer nanocomposites is gener-ally governed by several factors, purification of CNTs to remove certain impurities such as amorphous and metallic carbon, optimal CNTs' dispersion, CNTs curvature and controlled content ratio of CNTs in the nanocomposite are of major significance in the performance of CNTs/polymers nanocomposites. Besides this, the optimal performance of the CNTs/polymer

nanocomposites is also decided by the selection of suitable polymers as well. These performance parameters of the CNTs/polymer nanocomposites are generally evaluated in terms of the inter-CNTs-polymer interaction. Study and sorting out of the interaction characteristics of the nanocomposite system have, therefore, primary significance [61–63].

Interaction between different constituents of the CNTs/polymer nanocomposites consists of following three classes [63–66];

a.   Interaction between nanotubes in a bundle,

b.   Interaction between different shells (in case of MWCNTs),

c.   Interaction between CNTs and polymer matrix.

In the CNTs/polymer nanocomposites, the constituents, that is CNTs and polymers preserve their original character both chemically and physically. However, they also deliver additional properties from combination. These added properties mainly depend on the following factors:

a.   Interfacial bonding between CNT and polymer,

b.   Mechanical load transfer from the polymer matrix to CNT, and

c.   Interfacial strength

Various investigations have proved that in case of insufficient load transfer (e.g. micromechanical interlocking, bonds, etc.) from the polymer matrix to CNT, the resultant nanocomposite display properties less than that of expected. Therefore, strong interaction between CNTs and polymer at their interface is one of the pre-requite condition for better mechanical performance of the nanocomposite. Additionally, the effective dispersion of CNTs in the polymer matrix has also vital significance in this context. Ultrasonication and refluxing are two means for such dispersion. Interfacial chemical bonding may be obtained by pre-functionalization of CNTs which offers a strong interface and leads to effective stress (load) transfer. However, it must be noted that only non-covalent functionalization is supporting in this effect, whereas covalent functionalization of CNTs is not suitable because it may disturb the covalent bonds of graphene sheet.

In order to evaluate such an interfacial interaction, computational methods are used. Molecular dynamics (MD)-based simulation has been used frequently due to its flexibility and being more accurate. This kind of MD simulation is based on two different approaches. In the first approach, a CNT is dragged out of the nanocomposite and in the second approach, a CNT and polymer units are fetched together for studying their interaction. Results of both types of approaches are evaluated in term of some technical parameters, which are given below [67–70]:

a.   **Interaction energy (Interfacial-binding energy):** This is obtained by taking the difference between potential energy of the nanocomposite and sum up of the individual ingredients (CNTs and polymers). It is denoted by E_{int} and is given by

$$E_{int.} = E_{nc} - \left(E_{CNT} + E_{polymer} \right) \tag{13}$$

If we divide $\mathbf{E_{int}}$ cross-sectional area of the CNT and normalize it by the number of polymer molecules, then we get the interfacial binding energy.

$$\left(B.E\right)_{interfacial} = \mathrm{Norm}\left[\frac{E_{int.}}{A_{CNT}} \right] \tag{14}$$

b. **Strain–strain curve and shear modulus:** It is defined as the work done, which is required to drag out a CNT divided by the cylindrical volume of the CNT.

$$\tau_{interfacial} = \frac{W_{dragout}}{\pi r^2 l} \tag{15}$$

where r is the external radius of the CNT and 'l' is its length.

3.4. CNTs/polymer composites for gas sensors

3.4.1. Working principle

After learning about the interfacial interaction in CNTs/polymer nanocomposites, we are now able to describe the device applications of these nanocomposite materials in the gas sensors. Such nanocomposite materials when synthesized for the gas-sensing systems, generally contains organic polymers as the major polymeric materials. However, there is no restriction on the use of conducting/non-conducting polymers. Both can be applied in the gas sensor system.

Conducting polymers possess semiconducting nature because of their heterocyclic compounds, which exhibit physicochemical characteristics. Such properties can lead to the reversible changes in the conductivity of the sensing layer, which can be readily observed when polar chemicals are adsorbed on their surface, even at room temperature [71]. Such a change in conductivity is based on the following two causes [72]:

a. By charge transfer between gas molecules and the polymer,

b. The swelling of polymer film.

Non-conductive polymers can also be used as gas-sensing materials. In spite of the conductivity changes, the bulk dissolution of gas into the film may change their other physical properties [73], for example inside the polymer-coated resonators (by Avramov et al. [74] and Yantchev et al. [72]). Conducting particles-insulating matrix composition is another nanocomposite used as gas-sensing materials where the polymer acts as the insulating matrix, while the dispersed conducting particles provide the conducting path for sensing [75]. Due to the adsorption of interested analyst, there are volumetric changes of the matrix polymer. CNTs, due to its one-dimensional structure and good conductivity, are ideally used as the dispersed particles in this conducting particles-insulating matrix composition for gas-sensing systems. Due to this fact, CNTs/polymer composites have been widely studied for gas sensors [76–78].

3.4.2. Sensing mechanism

Interfacial bonding between CNTs and polymer executes main contribution to the gas-sensing effect of such nanocomposites. However, on the basis of experiments, following common sensing mechanisms have been suggested.

a. Due to the occurrence of quantum mechanical tunnelling effects, conducting paths are formed inside the CNT/polymer composites and the distance between these conducting paths is such that hopping of electrons between them occurs. With the increase in distance between the adjoining carbon nanotubes, their mutual contact resistance between them increases. After the polymer nanocomposites are exposed to target gas, adsorption of organic vapours leads to the swelling of the polymer matrix that increases the volume, and hence the distance between adjoining nanotubes. Consequently, the contact resistance increases too. This entire dependency of all the parameters, particularly (the coverage of swelling and resultant electrical response) mainly depends on the polymer's solubility in the solvent. Such a mechanism was initially suggested in the literatures [79–82].

b. Another mechanism is based on the charge transfer due to the adsorption of polar organic molecules which affects the electronic properties of the semiconductor CNT surface. Such an adsorption of gaseous molecules is mainly due to the fact that the nanocomposite's surface and solvent molecule both exhibit polar nature. The attached polar functional groups to the CNT surface adsorb solvent molecules. Polarity of gaseous molecules decides the ability of the sensing response. More polar is the adsorbed molecule, quick response is there, and vice versa. Similarly, the polar groups on the CNTs' surface also increase directly with the adsorption of solvent molecules, and hence, a better response is obtained. This fact has been observed for CNT/PMMA nanocomposites with polar solvents like methanol which showed an improved response to f-CNT/PMMA composites even though they are not good solvents for PMMA [83, 84]. It was observed that the reversibility of these sensors with such polar solvents is very poor. This means that even though the sensor is re-exposed to air, the resistance value does not return to its initial value completely, that is the polar interaction between the CNT surface and these solvents is high so that desorption from the surface is slow [85].

3.5. Literature survey

Due to their exclusive and remarkable properties, CNT/polymer nanocomposites-based gas sensors are the focus of recent gas sensor research. Aim of the entire efforts is to lower the working temperature and enhance the sensing parameters such as sensitivity, response speed and selectivity. Earlier, An et al. [86] prepared SWNT/polypyrrole nanocomposite by in situ polymerization of the pyrrole and SWMTs mixture (**Figure 13**).

Gas-sensing device was fabricated through spin-casting on the already patterned interdigitated electrodes. Sensing response of this nanocomposite was investigated towards NO_2 gas which showed better sensitivity than the pure individual materials (CNTs or polypyrrole); however, the major drawback with this nanocomposite is that it degrades when it is exposed to the gas for longer time (**Figure 14**).
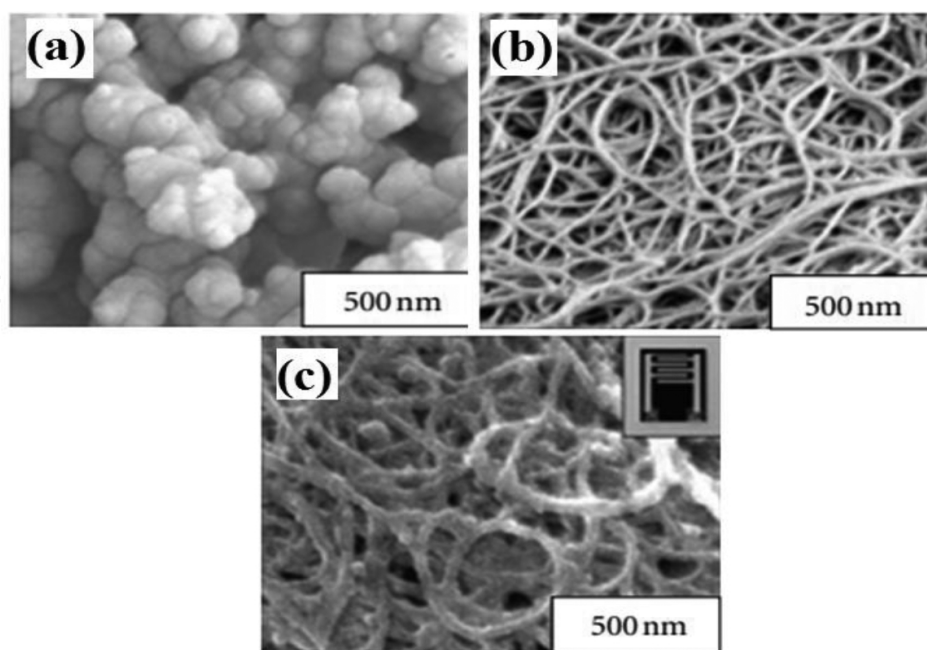
Figure 13. FESEM images of (a) pure Ppy, (b) pure SWNT bundles and (c) SWNT/Ppy nanocomposite. Inset: optical microscope image of the interdigitated electrodes.
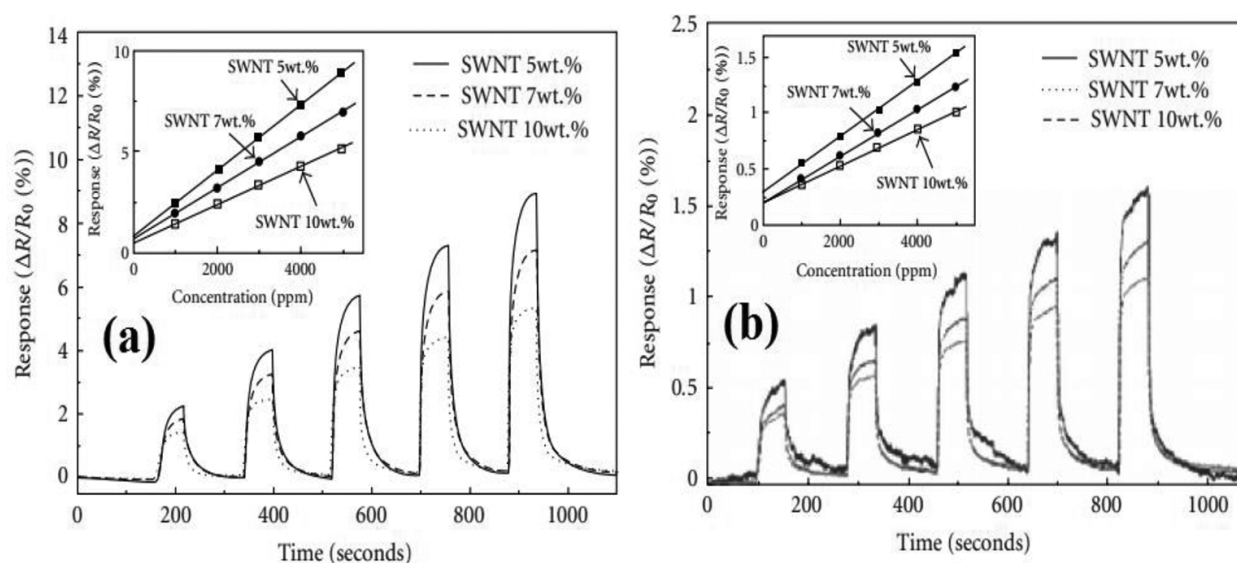

Figure 14. The change in sensitivity as a function of gas exposure time for 3000 ppm NO_2.

Then Cho et al. [87] introduced SWCNT-ethyl cellulose (SWCNT/EC) nanocomposite. This nanocomposite was prepared by solution-blending process with the use of chloroform as media. The interdigitated electrode technique was used to fabricate the gas-sensing device, and its response was investigated towards benzene and ethanol. Resistance observed almost a linear variation with the gaseous concentration, and it gave reasonable sensitivity to both of the gases (**Figure 15**).
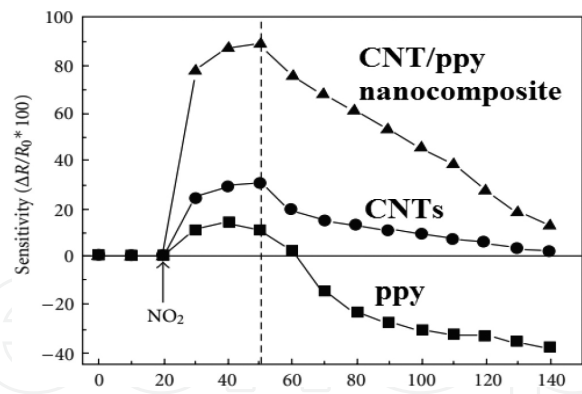
Figure 15. (a) Gas-sensing properties of SWNT–Polymer (EC) composites for 1000–5000 ppm benzene vapours, (b) gas-sensing properties of SWNT–Polymer (EC) composites for 1000–5000 ppm ethanol vapours (insets in the upper left corners show the linear relationship) [87].

Using similar idea, Philip et al. [85] prepared composite thin film of MWCNT/polymethylmethacrylate (MWCNT/PMMA) and functionalized-MWCNT/PMMA (f-MWCNTs/PMMA) nanocomposites. Their sensitivity response was investigated to a variety of gases (dichloromethane, chloroform, acetone, etc.). Both of nanocomposites response well; however, the enhancement in sensitivity and response time of f-CNT/PMMA composites was more significant (**Figure 16**).

In addition of CNT/polymer composite, the sensing characteristics of polymer-coated CNTs film (CNT as a major material) towards specific gases were also tested. Li et al. [88] studied the sensing character of this kind of structure by coating of polymer on CNTs. Chlorosulfonated polyethylene (polymer) was dissolved in tetrahydrofuran (THF) solvent, which was used as a coating solution for Cl_2 sensing, and hydroxypropyl cellulose was dissolved in the solvent chloroform as coating on SWCNTs to detect HCl. Both the nanocomposites responded well to the corresponding gases. **Table 3** tabulates familiar CNT-polymer nanocomposites, which have been investigated for gas sensors.
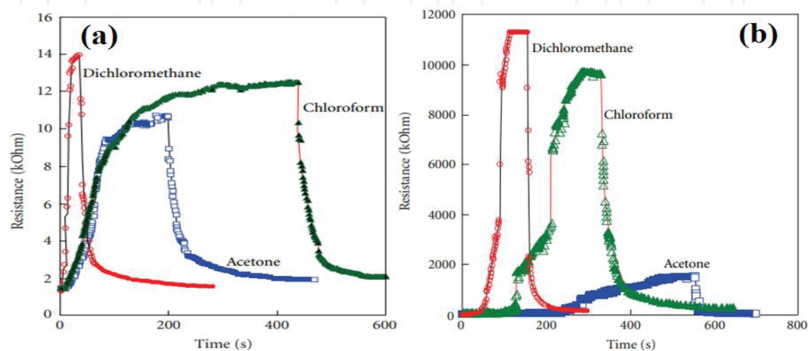

Figure 16. Response of (a) CNT/PMMA and (b) f-CNT/PMMA composites to dichloromethane, chloroform and acetone vapours [85].

Organic polymer	CNT type	Sensor configuration	Targeted analytes	Functionalization method	Detection limit	Response time (s)	Reversibility
PEI, Nafion	SWNTs	ChemFET	NO_2, NH_3	Non-covalently drop-coating	100 ppt (NO_2)	60–120	Reversible (UV)
PMMA	MWNTs	Chemiresistor	Dichloro methane, chloroform, acetone	Mixed as composite film	N/S	2–5	Reversible
PEI/Starch mixture	SWNTs	ChemFET	CO_2	Non-covalently dip-coating	500 ppm	60	Reversible
PEI	SWNTs	ChemFET	NO	Non-covalently drop-coating	5 ppb	70	Reversible
Polypyrrole	SWNTs	ChemFET	NO_2	Covalent chemical polymerization	N/S	600–1800	Reversible
Poly(3-methylthiophene)	MWNTs	Chemiresistor	CH_2Cl_2, $CHCl_3$, CCl_4, CH_4	Covalent chemical polymerization	N/S	60–120	Reversible
PABS	SWNTs	Chemiresistor	NH_3, NO_2, H_2O	Covalent chemical functionalization	20 ppb (NO_2), 100 ppb (NH_3)	600	Reversible
Poly(vinyl acetate), Polyisoprene	MWNTs	Chemiresistor	Tetrahydrofuran, ethanol, cyclohexane	Non-covalently drop-coating	N/S	1200	Reversible
Polyaniline	SWNTs	Chemiresistor	NH_3	Non-covalent electrochemical functionalization	50 ppb	600	Reversible
Polyaniline	MWNTs	Chemiresistor	Triethylamine	*In situ* polymerization (PANI–SWNT composite)	500 ppb	200–400 (up to 600 for recovery)	Reversible

Table 3. Some well-known CNT-polymer nanocomposite materials investigated for gas sensors [89].

Likewise, we had prepared polystyrene/MWCNTs nanocomposite through solvent evaporation technique and investigated improvement in its electrical properties and thermal stability, which is quite reasonable [90].

4. Conclusion

In summary, the gas sensors based on both CNTs (in single and bundle form) and CNT/polymers nanocomposites are being focused to lower the working temperature, enhance response speed and sensitivity. However, the problem of their degradation during exposure for longer times or high temperature is still to be resolved. Efforts in this line are in continuous run. Exploration of new and novel nanocomposite materials of polymers with CNTs is increasing day by day, which will indeed sort out solution to unresolved technical and industrial issues.

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