

Recent development in carbon nanotubes based gas sensors

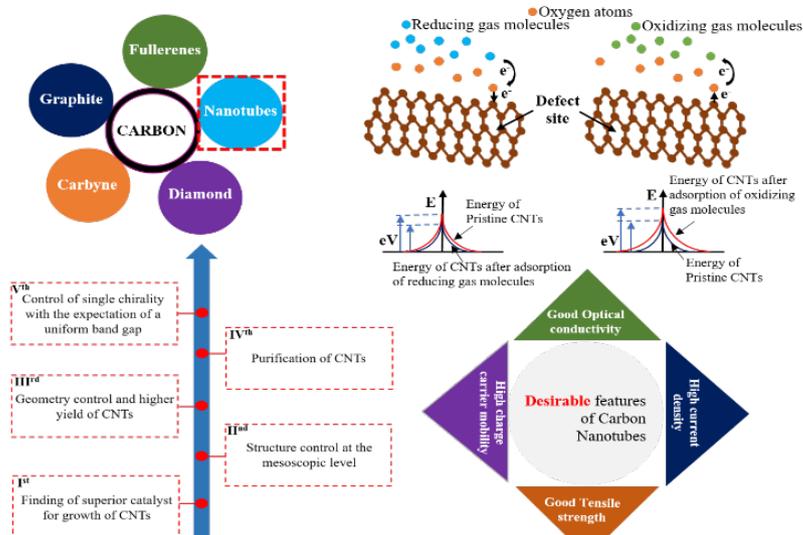
Gulshan Verma, Ankur Gupta*

Department of Mechanical Engineering, Indian Institute of Technology Jodhpur-342037, India

Submitted on: 29-Oct-2021, Accepted and Published on: 18-Feb-2022

Review

ABSTRACT Technological expansion in nanotechnology has given an upsurge to a new generation of functional organic nanomaterials with well-defined characteristics and controlled shape, allowing for a large number of possible applications. Innovative detection systems for the reliable and timely monitoring of dangerous gases in industrial processes and the environment are vital for maintaining optimum health and safety. Carbon-based gas sensors are becoming increasingly popular due to their unique characteristics and high sensitivity. Carbon nanostructures, such as carbon nanotubes (CNTs) are generally recognized as prospective nanomaterials for developing a new gas sensor with important nanotechnology implications. CNTs in particular have fueled the development of gas sensors that take advantage of their unique morphology, greater surface-area-to-volume ratio, chemical inertness, nanoscale architecture, and hollow core; all of this makes these materials appealing for current nanotechnology applications as well as one of the potential future generation materials. This review work covers the current state-of-the-art work on electrical and electronic properties; sensing mechanisms, and recent advancements in gas sensors development based on organic nanomaterials; carbon nanotubes in particular.



Keywords: CNTs, gas sensor, sensing mechanisms, carbon nanostructures.

INTRODUCTION

Exposure to various pollutant gases has been upheld to be unswervingly harmful to the health of the exposed people. Nitrogen oxides, VOCs, hydrogen sulfide, and carbon monoxide are recognized to be the most dangerous gases.¹ Monitoring air pollutants necessitates the use of high-performance sensors capable of identifying and measuring gaseous and vaporous species. Furthermore, using an electronic gas measurement method for mobile and on-site monitoring is highly recommended². The current state of nanotube research is marked by a keen interest in their synthesis techniques, properties studies, and attempts at industrial use. Nanostructures can be made in a variety of dimensions, including 0-D, 1-D, 2-D, and 3-D.³⁻⁵ Quantum dots, for example, have been used as a structural element including optical sensors, quantum lasers, and memory

modules. Nanowires metal oxides, carbon nanotubes, and organic semiconductors have all been employed as gas sensors in the past.⁶⁻⁸ Experiments have also been conducted on various sensing materials, the properties of which allow for high sensitivity and rapid response towards a specific gas.^{9,10} One of the most significant breakthroughs of advanced science is the discovery of carbon nanotubes (1D nanostructures). This stage of carbon's existence falls between graphite and fullerenes.¹¹ Many of the features of nanotubes, on the other hand, are vastly different from those of the carbon forms discussed above. CNTs are used in a variety of applications, including electron emission in automobiles¹² for cathode rays from lighting components, gas discharge tubes, lithium battery anodes, flat panel displays, in telecommunications networks, biosensor face mask materials,¹³ energy conversion, electromagnetic wave absorption, and shielding, composite materials, and hydrogen storage.^{14,15} Carbon nanotubes are promising materials with distinctive traits such as a large aspect ratio,¹⁶ mechanical stability, and excellent electrical conductivity. Because of their adsorption capability and large surface area, carbon nanotubes are intriguing as gas sensing materials.¹⁷ Carbon nanotubes have been proposed for use in a variety of gas sensors. When ionizing the target gas using field

*Corresponding Author: Dr. Ankur Gupta
Email: ankur Gupta@iitj.ac.in



URN:NBN:sciencein.jmns.2022.v9.282
© ScienceIn Publishing ISSN: 2394-0867
<https://pubs.thesciencein.org/jmns>



emission electrodes with CNTs in a gas ionization sensor, high sensitivity and selectivity are observed.¹⁸ Figure 1 shows the various crystalline structure of carbon. CNTs have been the focus of many disciplines and even multidisciplinary fields of study since their scientific breakthrough in 1991 due to their distinct physical and chemical properties.¹⁹ CNT-based gas sensors, in particular, have attracted much interest because of their outstanding characteristics.

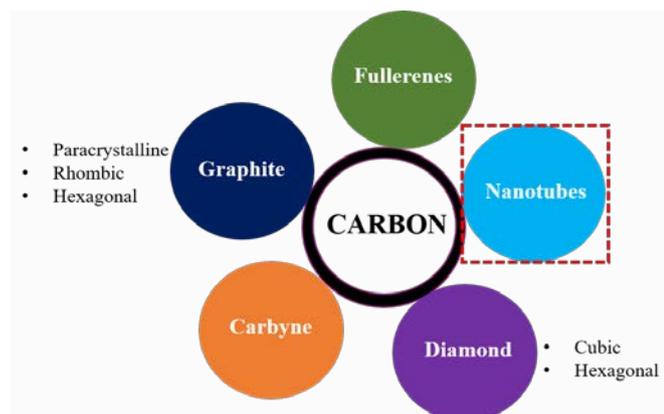


Figure 1. The various crystalline structure of carbon.

Single-walled carbon nanotubes (SWCNTs) are made up of a single graphite sheet that has been seamlessly wrapped around a cylindrical tube, whereas multi-walled carbon nanotubes (MWCNTs) are made up of an array of these nanotubes.²⁰ The gas sensor mechanism from another study is based on the change in electrical conductivity of carbon nanotubes.²¹ Similarly, other studies show that developing carbon nano-horns as a gas detecting material can improve sensitivity. The conductivity of SWCNTs is affected by the transfer of charge between the adsorbed gas molecules and surface SWCNTs. At room temperature, this sensor should have a quick response, high sensitivity, and compatibility with ICs. The adaptability of carbon nanotubes in various applications makes them a promising option for future study in order to meet ever-increasing application demands. The electrical performance of carbon nanotubes-based devices is widely known to be highly sensitive to the chemical environment in which they function. From a practical standpoint, it is critical to conduct a thorough investigation into the interaction of carbon nanotubes with gases,

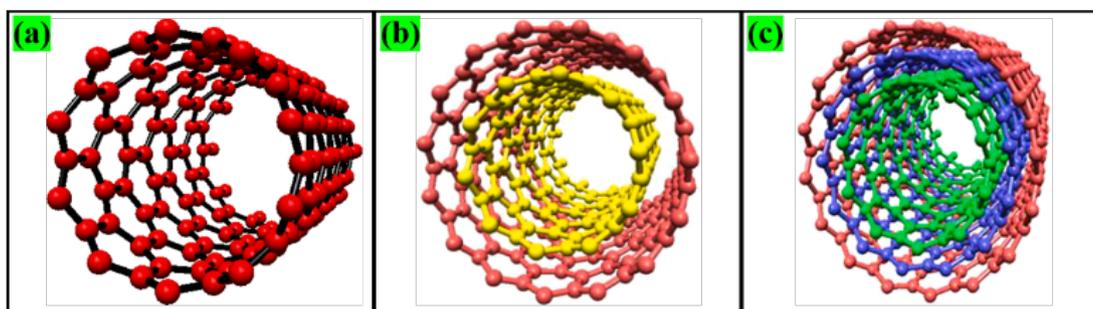


Figure 2. Surface and internal view of single, double, and multi-walled CNTs.²² (Reproduced with kind permission from ref [22]).

since this will considerably improve the understanding of the physics of nanoscale devices made of these materials. Figure 2 shows the surface and internal view of single, double, and multi-walled CNTs.²² CNTs have proven to be a useful sensing material for sensor applications at the nano-levels having a larger surface-to-volume ratio. Furthermore, a wide spectrum of research in this area has resulted in the fabrication of flexible and portable room temperature gas sensors based on nanotubes, as well as the demonstration of practical uses of CNTs through functional electronic devices.^{23,24} Figure 3 shows the various stages in the synthesis of carbon nanotube research.

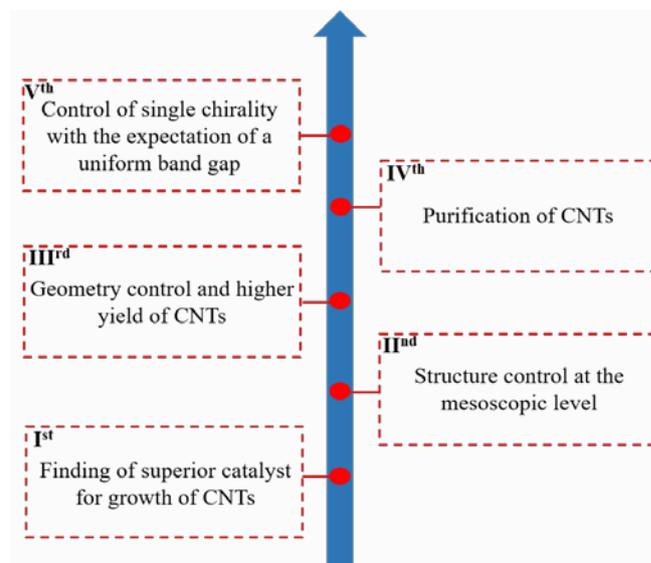


Figure 3. Phases in the synthesis of CNTs research.

Because carbon nanotubes are not found in nature, they must be made in the laboratory utilizing a variety of procedures and experimental circumstances. Laser ablation, ball milling, electrolysis, arc discharge, CVD, and other processes are among them. The mechanism and properties of CNTs growth are controlled by process factors such as pressure, gas flow rate, reaction time, carrier gas, catalyst concentration and size, growth temperature, substrate, and type of carbon precursor in each CNTs synthesis procedure. The stated process parameters must be harmonized in order to get a pure, well-structured, and superlative carbon nanotube. This study covers the current state-of-the-art work and advancements in gas sensors development based on carbon nanotubes.

ELECTRICAL AND ELECTRONIC PROPERTIES OF CARBON NANOTUBES

The electrical characteristics of CNTs have been studied extensively. CNTs can be employed as junctions between metals, semiconductors, and metallic metals because their electrical characteristics are dependent on the tube structure.²⁵ The band structure of graphene can be used to understand the electrical characteristics of carbon nanotubes. The anti-bonding (π^*) and bonding (π) orbitals degenerate at Fermi-points in the Brillouin zone, as seen in the graphene dispersion relationship (see figure 4(a)). The conduction and valence bands are coupled to each other at the Fermi points, and the graphene bandgap is zero at these places, making graphene a zero-bandgap semiconductor. Each graphite band in carbon nanotubes opens up to form a number of sub-bands because of the confinement of electrons in the radial direction. Carbon nanotubes are metallic, as shown in figure 4 (b) if the sub-bands of CNTs pass via Fermi points, otherwise, they are semiconductors, as shown in figure 4 (c).²⁶

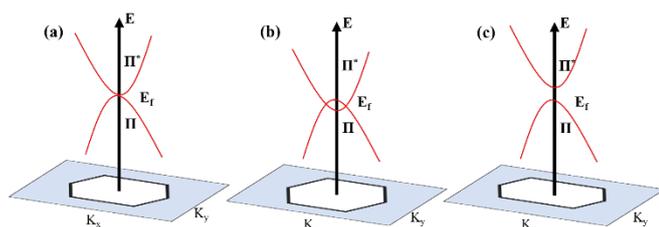


Figure 4. Dispersion relations of (a) graphene (b) metallic nanotubes (c) semiconducting nanotubes.

The CNTs generated at the armchair are either zigzag or chiral, depending on the orientation of the axial wrapping. Armchair or zigzag carbon nanotubes are generated by rolling the graphene sheet along the axis of symmetry; otherwise, chiral carbon nanotubes are formed. For armchair CNTs, the circumferential vector (C) is exactly in the direction whose chiral indices are $n = m$ with a chiral angle of 30° . The resulting nanotubes are entirely metallic. In zigzag CNT, however, the circumferential vector can only be obtained along with one of the two fundamental vectors, i.e. one of the chiral indices is zero out of n or m with the chiral angle is 0° . The chiral type CNTs are formed when the chiral angle follows the relation, $0^\circ \leq \theta \leq 30^\circ$ and for $m \neq n$. Bend-induced energy gaps in CNTs with $n-m = 3j$ (where j is an integer) are typically on the order of a few meV. CNTs with $n - m = 3j$, on the other hand, exhibit an energy gap bigger than 1 eV. During the manufacturing of semiconductor carbon nanotubes, the bandgap can be adjusted. The energy gap is proportional to the diameter of SWCNTs at $E_{gap} = 0.7/d$ (eV)^{27,28}. Figure 5 shows various shapes of SWCNTs. Table 1 shows an example of a different form of functionalization on CNTs.

CNTs with a length of up to a few microns have length-independent conductivity, which is a benefit in the preparation of ballistic conductors. Strong covalent bonding and the 1-D structure of CNTs decrease small-angle scattering caused by imperfections and lattice vibrations. Only electrons are allowed to flow back and forth in CNTs. Electron backscatter events in

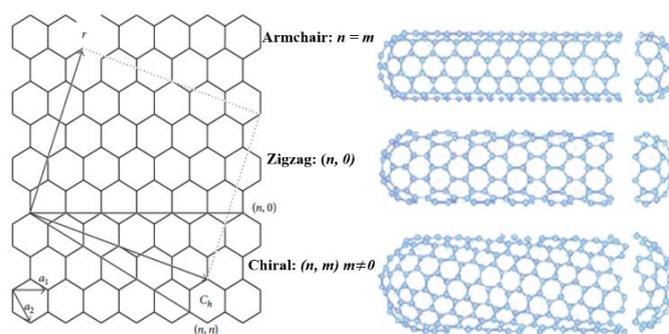


Figure 5. Representation of armchair, zigzag, and chiral-shaped SWCNTs.²⁸ (Reproduced with kind permission from ref [28]).

Table 1. Various functionalization on carbon nanotubes.

CNT Functionalization		
Covalent functionalization: The sidewalls of CNTs are covalently functionalized, changing their hybridization from sp^2 to sp^3 .		Sidewall Functionalization. ³⁰
		Defect Functionalization. ³¹
Non Covalent functionalization: To generate a perfect Nanotube structure, this kind of functionalization includes π -stacking interactions, weak van der Waals forces, H_2 bonding, and electrostatic force.		Wrapping of DNA, polymer or protein, etc. on carbon nanotubes. ³²⁻³⁴
		Endohedral Functionalization. ³⁵

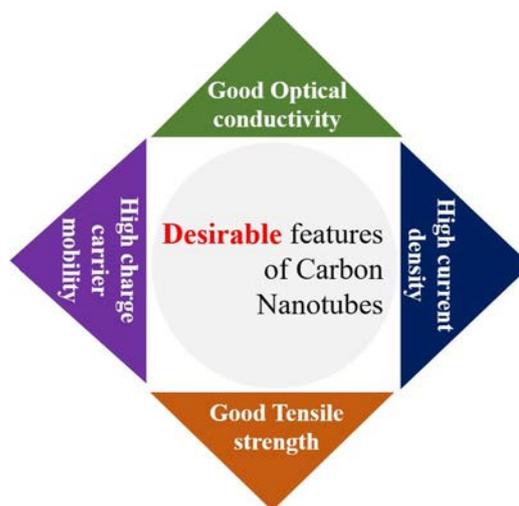


Figure 6. Desirable properties of CNTs.

CNTs are decreased because they have a symmetrical band structure.²⁹ Figure 6 shows the various desired features of CNTs.

ADSORPTION SITES FOR GASES ON CARBON NANOTUBES

The density functional theory (DFT) and first-principles calculations are used to explain the adsorption of various gas molecules in CNTs. Tube-molecule spacing, binding energy, and transfer of charges are all investigated in general. This approach was utilized by Peng et al.³⁶ to explore the adsorption of nitrogen dioxide in SWCNTs. Figure 7 depicts the SWCNTs bundle concept, which displays four different spots where gas molecules are generally adsorbed. (a) the outer surface of SWCNTs bundle; (b) groove created at the bundles outside surface when in contact between adjacent tubes; (c) interstitial channel; and (d) interior pore. The adsorption of gas molecules in these locations is dependent on the availability and diameter of sites; the size of gas molecules; and the binding energy of molecules.³⁷ Even though there are many potential adsorption sites, many gas molecules may only be adsorbed on a few due to their unique features. At 133 K, one of the disintegrated components of SF₆, Carbon tetrafluoride could be adsorbed at the outer centers of closed SWCNTs as well as on the inner and outer sides of open SWCNTs but SF₆ could only be adsorbed on the outside surface.^{38,39}

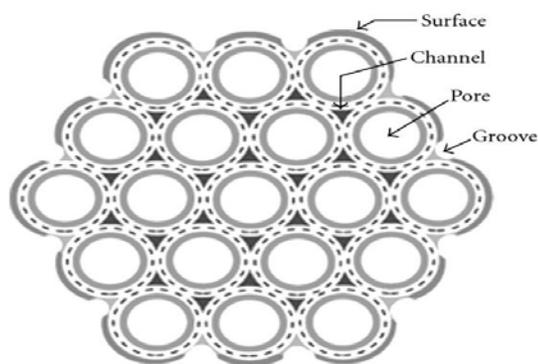


Figure 7. Schematic view of available adsorption sites on carbon nanotubes.³⁷ (Reproduced with kind permission from ref [37]).

Calbi et al.⁴⁰ investigated energy barriers and adsorption sites near the ends of CNTs bundles to analyze the impact of gas molecule adsorption in the interstitial channels between the tubes. They came up with two primary findings. The first is that the capacity of interior locations and groove locations are inversely related to the volume occupied by the molecule and the length of the adsorbed molecule, respectively. Secondly, adsorption in the outside grooves is significantly faster than in the interstitial channels. Because the adsorbed gas molecules are directly exposed at the carbon nanotube's external locations, where the adsorption process begins and then diffuses to the internal regions.⁴¹ As a result, it's not unexpected that adsorption at exterior locations equilibrates significantly more quickly than adsorption at interior locations at the same pressure and temperature conditions.

Adsorption energy (E_{adsorp}) corresponding to each adsorption site are expressed as followed:

$$E_{adsorp} = E_{nanotube/molecule} - E_{nanotube} - E_{molecule}$$

The higher the adsorption energy, the more difficult the adsorption will be; on the other hand, the more negative the value of E_{adsorp} , the more spontaneous the process will be, which roughly conforms to the aforementioned equation.

According to Williams et al.⁴² adsorption energy between the hydrogen gas molecule and carbon nanotubes in various locations follow the following sequence; E_{adsorp} (interstitial-channels) > E_{adsorp} (outside-grooves) > E_{adsorp} (interior-pores) > E_{adsorp} (outside-surfaces).

CHEMIREISTIVE BASED GAS SENSING MECHANISM OF CNTS

Carbon nanotubes are used as a gas sensing material due to their high surface/volume ratio, porous structure, and presence of defect sites, this provides the gas molecules with a vast number of binding sites. CNTs are durable in a variety of reaction conditions due to their great thermal stability, which allows them to preserve their intrinsic structure. The elimination of the no loss of power, thermal element, easy design of the sensor, downsizing, are some of the benefits of using CNT-based sensing material. The biggest disadvantage of operating at room temperature is the possibility of humidity influence. When the target gas from the environment is deposited on the surface of the CNTs, charge transfer happens between the carbon nanotubes and the gas molecules. The upper layer atoms in CNTs are of considerable importance because adsorption is a surface phenomenon. All atoms in SWCNTs behave like surface atoms,⁴³ the sensor response is controlled by the atoms in multi-walled carbon nanotubes (MWCNT's) outermost layer.⁴⁴ CNTs come in contact with target gases in one of two ways: (i) Van der Waals interactions and, (ii) donor-acceptor interactions. The sensing mechanism of CNTs based gas sensors is gas adsorption-induced charge transfer. CNTs behave like p-type semiconductors due to the formation of defects and oxidation states during synthesis and purification. The type of absorbing gas influences the transport of electrons to and from carbon nanotubes. The resistance value of CNTs⁴⁵ increases when they interact with reducing gases because of the combination of free holes (provided by the nanotubes) and electrons (supplied by the gas molecules). Similarly, when oxidizing gases adsorb onto the surface of carbon nanotubes, electrons are removed. The removal of electrons from carbon nanotubes increases the population of holes in the CNTs, lowering the sensor's output resistance⁴⁶. CNTs-based gas sensing responses are influenced by three factors: inter-CNTs, intra-CNTs, and modulations of schottky barrier.² For SWCNTs and MWCNTs, the intra-CNTs gas sensing mechanism involves interactions between the target gases and individual and bundles of nanotubes, respectively. The overall electrical characteristics of a CNTs network are affected by the inter-tube conduction system (inter-CNTs). SWCNTs-based sensors have a higher response than MWCNTs-based sensors attributed to the prevalence of more defect sites. Figure 8 shows the transfer of an electron from CNTs and the adsorbed reducing and oxidizing gas molecules.

Another phenomenon that affects the response of sensors is heteroatom doping of CNTs. In carbon nanotubes, chemical doping involves replacing carbon atoms with heteroatoms like

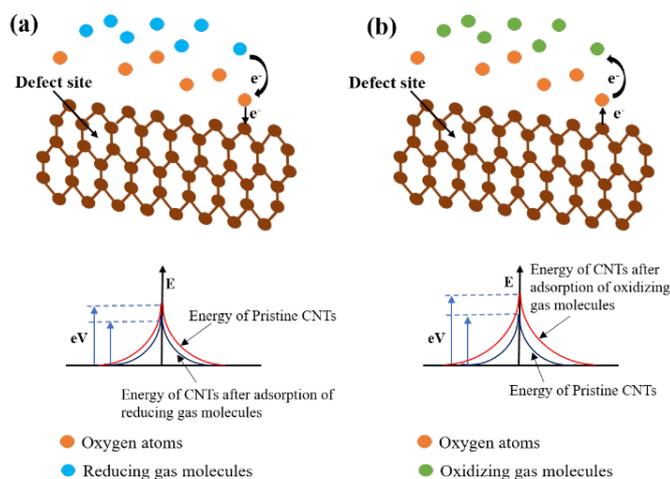


Figure 8. The electron transfer mechanism between adsorbed (a) reducing and (b) oxidizing gas molecules, and carbon nanotubes.

Table 2. Advantages and disadvantages of various carbonaceous materials.

Carbonaceous materials	Advantages	Disadvantage
Carbon black	There are a lot of defective sites, and the chemical inertness is good.	Inadequate conductivity, insufficient pore size, and surface area
Amorphous porous carbon	a large surface area, a sophisticated porous structure, a large number of defective sites, and high chemical inertness	Poor adhesion with FTO due to low conductivity
Carbon nanotube	Chemical inertness, large surface area, and high electrical conductivity	Sites with a low number of defects
Carbon nanofiber	Mechanical strength, thermal conductivity, and chemical inertness are all advantages.	Inadequate porous system and surface area; and insufficient conductivity
Graphite	Excellent thermal stability, good conductivity, and corrosion resistance	Low surface area, poor porous system
Graphene	Excellent mechanical strength and conductivity, rapid charged carrier movement, excellent optical transparency, and mechanical inertness are all advantages of this material.	The low surface area due to simple aggregation, and low numbers of defective sites

nitrogen and boron. Doping changes the chemical and physical properties of carbon nanotubes in the vicinity of the dopant atom, increasing the binding energy of gas-molecule interactions. Table 2 shows the advantages and limitations of carbonaceous materials.

RECENT ADVANCEMENTS IN THE CNT'S BASED GAS SENSORS

Kawano et al.⁴⁷ created a novel gas sensor that detects both gas and its pressure using the electrothermal action of MWCNTs. As shown in Figure 9a, MWCNTs were fabricated on a Si wafer using CVD technology and suspended between two Si microstructures utilizing an electrical feedback system. Through conduction and radiation, the heat was discharged into the environment, affecting MWCNTs' ability to detect gaseous species. MWCNTs have a thermal conductivity of 0.137% K⁻¹. When detecting N₂ and Ar gases at different pressures, the thermal conductivity of the MWCNTs was recorded as 25.83 and 17.72 W/mK, respectively. Moreover, by reducing the length and contact area, the performance of CNTs based gas sensors can be improved. Figure 9(b) shows how the voltage shifts when CNTs are placed across Si microstructures; as the voltage increases, it becomes easier to predict the number of effective CNT connections using the voltage vs time graph. Samples A and B (figure 9(c)) shows that MWCNTs connections are synthesized in 8 and 20-50 sec, respectively. Figure 9(d) shows the SEM views of single MWCNTs synthesized with a 25 micron length.

Pensa et al.⁴⁸ described a miniaturized sensor module that used modified (metal) and unmodified carbon nanotube to measure landfill gases at 150°C. Using a CVD method and high-frequency plasma, vertically aligned carbon nanotubes (VACNTs) with a 10 m length and a diameter of 535 nm, were produced on a Fe-coated aluminum substrate. The metals had particle sizes in the 550 nm range and occupied the upper surface of the VACNTs to provide chemical resistance for monitoring nitrogen dioxide in landfills. At room temperature, pure VACNTs and metal-modified VACNTs had electrical resistances of 100 to 120, 100 to 1000 ohms, respectively. For the concentration of 0.33 to 33 ppm, the metal-modified VACNTs is more responsive than the pure VACNTs. As gas sensors, both pure and metal-modified carbon nanotubes offer a wide range of uses. Abdulla et al.⁴⁹ used MWCNTs in combination with polyaniline (PANI) to detect levels of ammonia. On the outside walls of the MWCNTs, a 7 nm thick PANI layer was created. MWCNTs produced on an oxidized Si substrate are used in ethanol gas sensors⁵⁰. The CNTs had an average diameter and length of 45 nm and 4.52 nm respectively. The response of the gas sensor towards ethanol was recorded as 0.18 %, 0.41 %, 0.78 %, 1.20 %, and 1.67 % for 50, 100, 200, 400, and 800 ppm, respectively. Zhou et al.⁵¹ recently developed an SWCNTs-poly(9,9-dioctyl-fluorene) based semiconductor nitrogen dioxide based sensor. Nitrogen dioxide (NO₂) is recognized to be an oxidant since it has an unpaired electron. As a result, during NO₂ adsorption, NO₂ molecules push electrons away from semiconductor SWCNTs, the number of hole carrier's increases, resulting in thin SWCNTs films becoming weaker. Ghanbarian et al. developed a unique, low-cost, simple, and long-lasting resistance sensor built of MIL53

(Fe-Cr) / Ag NPs / CNTs for detecting VOCs (such as propanol, methanol, etc.) at concentrations ranging from 10 to 500 ppm. The size and shape of the particles, as well as their morphology, are known to have a significant impact on the sensor's performance.⁵² Due to the availability of high conductivity CNTs materials, CNT-containing CPC architecture demonstrated a suitable high signal-to-noise ratio and the capacity to detect VOCs analytes in the ppb range. Following that, the CPC precursor would be sprayed using a spray cannon. The spray approach has the benefit of deposition of film across a vast area on a variety of substrates.

After interaction with VOCs vapors, the CNT-containing CPC structure expanded, and a significant shift in sensor resistance occurred due to changes in the connection properties of the MWCNTs conductive networks.⁵³ The information from the TEM images depict the tube lengths and diameters of Pristine MWCNTs which is 0.2-0.16 μm and 40 nm, respectively with the inner gap of 5 nm, and the wall thickness of 15 nm. The TEM images also depict the presence of a small agglomeration of PVA. Similarly, in another study SEM images of the hollow structure of ZnSnO_3 . The existence of multiple shattered hollow boxes demonstrates the hollow shape. Each ZnSnO_3 hollow box is approximately 30 nm thick and 150 nm long. The morphology of CNTs (average diameter of 8 nm) decorated ZnSnO_3 square. The CNTs were uniformly attached to the ZnSnO_3

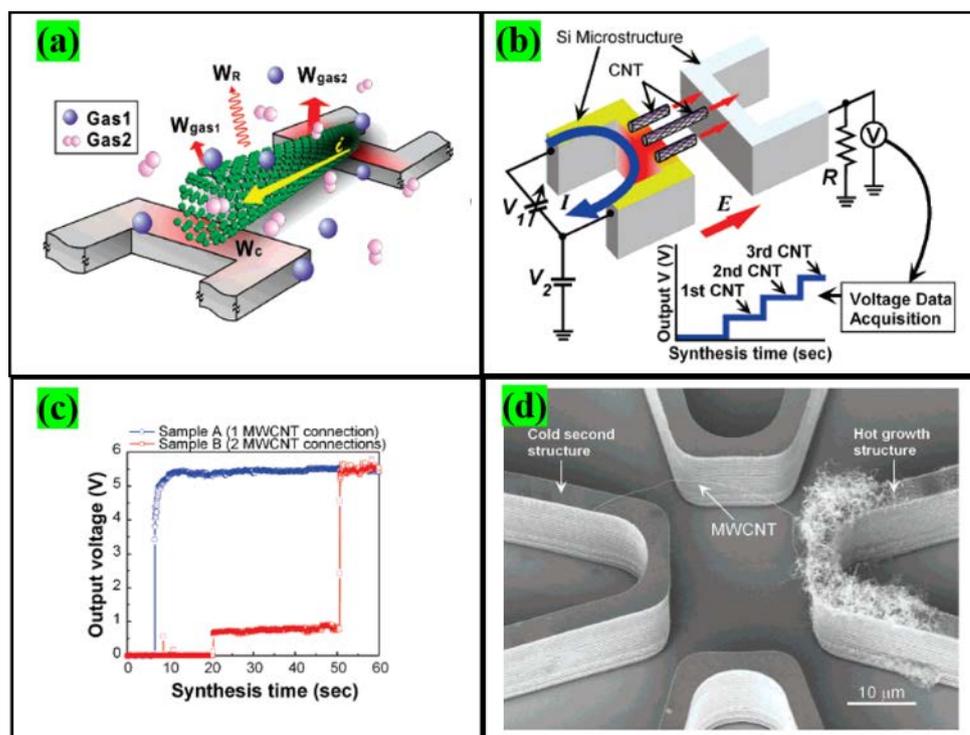


Figure 9. (a) A schematic depicting the methods of suspended carbon nanotubes gas sensing, (b) CNTs assembly by e-field guided chemical vapor deposition, (c) output voltage vs synthesis time for two MWCNT samples, and (d) scanning electron microscope view of MWCNTs based electrothermal gas sensor.⁴⁷ (Reproduced with kind permission from ref [47]).

Table 3. Summary of recently published work on CNTs based gas sensors.

Materials	Operating range (ppm)	Response time (sec)	Target gas	LOD (ppm)	Ref
Pd-SWCNTs	1-50	88.2	H ₂	1	61
Au-CNTs	40-200	37.50-39.78	H ₂	40	62
Pd-MWCNTs	100-500	30	H ₂	100	63
Au-SWCNTs	40-100	13	NO ₂	40	64
Pt-SWCNTs	1-3	282-294	NO ₂	1	65
Hydroxyl propyl cellulose-SWCNTs	0.025-0.3	300	NO ₂	0.025	66
PTh-SiO ₂ -SWCNTs	0.01-10	20	NO ₂	0.01	67
Au-Pt-MWCNTs	0.1-10	120-180	NO ₂	0.1	68
PMMA-SWCNTs	1-500	600	NH ₃	1	69
Co-MWCNTs	14-800	30-50	NH ₃	14	70
ZnO-CNTs	25-100	12.5	Methanol	25	71
CNTs-ZnO/PS	500-1000	18	Ethanol	500	72
Pd-MWCNTs	10-10000	920-1249	H ₂ /Ar	10	73
Al-MWCNTs	50-450	53.7	CO ₂	50	74
Polyimide-CNTs	50-500	12	CO ₂	50	75
In ₂ O ₃ -MWCNTs	10-250	9	Acetone	10	76
Fe ₂ O ₃ -CNTs	80-500	4	Acetone	80	77
MWCNTs-SnO ₂	2.5-5	67	Acetone	2.5	78
3D TiO ₂ -G-CNTs	50-500	10	Toluene	50	79

hollow box's surface, with no agglomeration. As a result, the CNTs are securely attached to the empty ZnSnO_3 box, forming a hierarchical structure.⁵⁴ A field-effect transistor (FET) was used in one of the studies to describe the use of SWCNTs to construct ultrasensitive sensors for the sensing of NO_2 gas.⁵⁵ The adaptability of these sensors is enhanced by their compact forms and low-temperature operation and at a low concentration of 100 ppb to 10 ppm. The Schottky barrier modulation is improved as a result of the device setup. SWCNTs were grown on Si/SiO₂ substrates in a horizontal tube furnace using a hot double filament aided CVD method. For values ranging from 0.05 ppm to 10 ppm, the change in resistance was measured. For almost four months, the sensor responses were consistent and repeatable. Sachan et al.⁵⁶ developed a quantum resistive vapor sensors (vQRS) nanocomposite with a hybrid copolymer of polystyrene, polymethyl methacrylate, polyhedral oligomeric silsesquioxane (POSS) with CNTs. Spray Layer-by-layer (sLbL) additive manufacturing is a useful control method for transducer's chemiresistive responses repeatability. There are two kinds of sensors that showed exceptional sensitivity to both dangerous chemicals in a dry environment, detecting CH_2O (300 ppb) and NH_3 (500 ppb) with a signal-to-noise ratio of 10. They also showed a fast response time for both vapors of less than 5 sec and could detect small amounts of gas (9 ppm formaldehyde and 1.5 ppm ammonia) even when there was 100 ppm water present. The current research demonstrates that electrostatic-layer-by-layer (eLbL) construction can help adapt the sensitivity of CNTs-polyelectrolyte sensors.⁵⁷

In another study, Shooshtari et al.⁵⁸ developed a vertically grown carbon nanotube-based sensor for sensing VOCs. Carbon nano-tubes based sensors are sensitive to humidity. The result shows the response of CNTs towards the introduction of relative humidity (RH) of 30%, 40%, 50%, and 70 % at ambient temperature. At room temperature, the adsorption period is virtually instantaneous because of the adsorption of molecules of H_2O onto the surface of carbon nanotubes. The desorption time, on the other hand, is longer. A water molecule can adsorb on the nanotube surface and between its walls. As the water content of nanotubes rises, adsorption on the surface becomes more prominent, and the water vapor shift promotes quicker desorption of H_2O molecules from the surface. The flexible fibrous gas sensors were developed using ZnO doped SWCNTs, SWCNTs, and MWCNTs in 2017.⁵⁹ These fibers are combined into a disposable nylon-based smart mask. When wrapped around a finger, the nylon fiber-MWCNTs demonstrated excellent

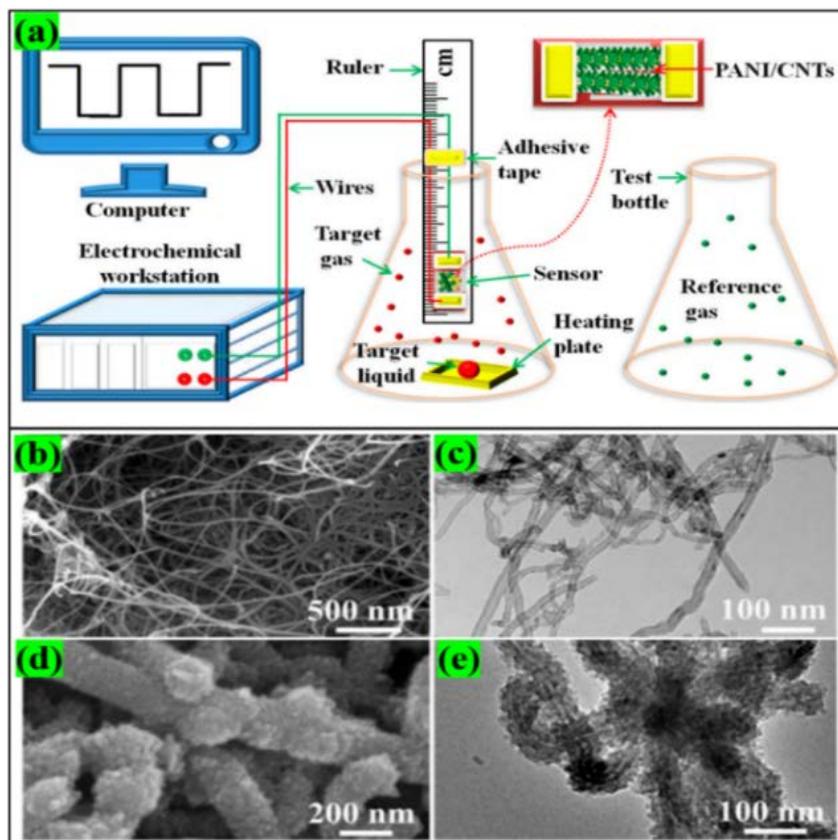


Figure 10. (a) Schematic of gas sensing setup for hierarchical PANI/CNTs fiber, (a, c) SEM, (b-e) TEM image of MWCNTs and n-PANI/CNTs fiber respectively.⁶⁰ (Reproduced with kind permission from ref [60]).

conductivity and flexibility. Zhang et al.⁶⁰ discussed the usage of polyaniline (PANI) to prepare MWCNTs. The detection qualities of the sensor were enhanced when they were heated before use. For 50 ppm NO_2 gas, the LOD and the response time were 16.7 ppb and 5.2 s, respectively. The reactions for the p-type PANI / MWCNTs and the n-type PANI / MWCNTs decreased by 19.1% and 11.3 %, respectively, over three months.

The type of conductive substance in the sensor affects the response of the gas sensor. The experimental setup is depicted in Figure 10(a). Figure 10(b-c) shows the SEM and TEM images of MWCNTs (10 nm diameter). Whereas, SEM and TEM images of a p-PANI/CNTs composite dried for 24 hours at 80 °C are shown in Figures 10(d-e). Table 3 shows the summary of the recent published works on carbon nanotubes based gas sensors.

SUMMARY

CNTs based gas sensors are the most researched devices to date, and they can detect a wide range of vapors and gases. The advantages of CNTs based gas sensors over standard metal oxide semiconductor (MOS) based gas sensors have been clear since the invention of the first CNTs based gas sensors. Since CNTs sensors can work at ambient temperature, the MOS-based sensors demand high temperatures and energy to operate. However, the lack of selectivity is the fundamental drawback of CNTs based gas sensors. There are still challenges to overcome before CNTs

can fully realize their potential in gas sensor applications. As structural instability is caused by low-dimensional shape and size. With greater strain, CNTs buck, kink, and collapse, so this is a vital challenge. Integrated circuits with real-time gas sensing that can detect, transform, process, and amplify small signals are being developed. However, the lack of selectivity remains the most significant impediment to the widespread adoption of these CNTs devices. As a result, greater efforts in this regard are required. The usage of carbon nanotubes in real products, on the other hand, is still in its infancy, but it has a bright future in the new industrial era.

ACKNOWLEDGMENTS

Authors would like to acknowledge the affiliating institute (IIT Jodhpur) to provide the research seed grant (I/SEED/AGK/20190022) which was helpful in understanding the reported work.

CONFLICT OF INTEREST

Authors declared no conflict of interest.

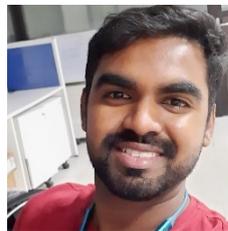
REFERENCES AND NOTES

1. A. Gupta, T. Sakthivel, S. Seal. Recent development in 2D materials beyond graphene. *Prog. Mater. Sci.* **2015**, 73, 44–126.
2. I. V. Zaporotskova, N.P. Boroznina, Y.N. Parkhomenko, L. V. Kozhitov. Carbon nanotubes: Sensor properties. A review. *Mod. Electron. Mater.* **2016**, 2 (4), 95–105.
3. A. Gupta, P.K. Parida, P. Pal. Functional Films for Gas Sensing Applications: A Review. In *Energy, Environment, and Sustainability*; Springer Singapore, **2019**; pp 7–37.
4. A. Gupta, S.S. Pandey, S. Bhattacharya. High aspect ZnO nanostructures based hydrogen sensing. *AIP Conf. Proc.* **2013**, 1536 (2013), 291–292.
5. P. Pal, A. Yadav, P.S. Chauhan, P.K. Parida, A. Gupta. Reduced graphene oxide based hybrid functionalized films for hydrogen detection: Theoretical and experimental studies. *Sensors Int.* **2021**, 2, 100072.
6. A. Gupta, S. Bhattacharya. On the growth mechanism of ZnO nanostructure via aqueous chemical synthesis. *Appl. Nanosci.* **2018**, 8 (3), 499–509.
7. A. Gupta, A. Srivastava, C.J. Mathai, et al. Nano porous palladium sensor for sensitive and rapid detection of hydrogen. *Sens. Lett.* **2014**, 12 (8), 1279–1285.
8. A. Gupta, S. Gangopadhyay, K. Gangopadhyay, S. Bhattacharya. Palladium-Functionalized Nanostructured Platforms for Enhanced Hydrogen Sensing. *Nanomater. Nanotechnol.* **2016**, 6.
9. N. Sheshkar, G. Verma, C. Pandey, A.K. Sharma, A. Gupta. Enhanced thermal and mechanical properties of hydrophobic graphite-embedded polydimethylsiloxane composite. *J. Polym. Res.* **2021**, 28 (11), 1–11.
10. V. Kishnani, G. Verma, R.K. Pippara, et al. Highly sensitive, ambient temperature CO sensor using tin oxide based composites. *Sensors Actuators A Phys.* **2021**, 332, 113111.
11. Srishti Dehmiwal, M. Bahuguna. Graphene - properties, production and rising applications: A review. *J. Mater. Nanosci.* **2021**, 8 (2), 51–63.
12. G. Kumar Verma, M.Z. Ansari. Design and simulation of piezoresistive polymer accelerometer. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, 561 (1).
13. B.S. Chhikara, R. Kumar, Poonam, P. Bazard, R.S. Varma. Viral infection mitigations using advanced nanomaterials and tools: lessons from SARS-CoV-2 for future prospective interventions. *J. Mater. Nanosci.* **2021**, 8 (2), 64–82.
14. P. Verma, R.H. Goudar. Mobile phone based explosive vapor detection system (MEDS): a methodology to save humankind. *Int. J. Syst. Assur. Eng. Manag.* **2017**, 8 (1), 151–158.
15. P.R. Verma, M. Verma. Techniques for smart & innovative parking, critical observations and Future Directions: A review. *2015 Int. Conf. Control Instrum. Commun. Comput. Technol. ICCICCT 2015* **2016**, 431–437.
16. A. Pal, B.S. Chhikara, A. Govindaraj, S. Bhattacharya, C.N.R. Rao. Synthesis and properties of novel nanocomposites made of single-walled carbon nanotubes and low molecular mass organogels and their thermo-responsive behavior triggered by near IR radiation. *J. Mater. Chem.* **2008**, 18 (22), 2593–2600.
17. K. Mondal, B. Balasubramaniam, A. Gupta, A.A. Lahcen, M. Kwiatkowski. Carbon Nanostructures for Energy and Sensing Applications. *J. Nanotechnol.* **2019**, 2019, 10–13.
18. Y.D. Lee, W.S. Cho, S. IL Moon, et al. Gas sensing properties of printed multiwalled carbon nanotubes using the field emission effect. *Chem. Phys. Lett.* **2006**, 433 (1–3), 105–109.
19. S. Iijima. Helical microtubules of graphitic carbon. *Nature* **1991**, 354 (6348), 56–58.
20. R. Andrews, D. Jacques, D. Qian, T. Rantell. Multiwall carbon nanotubes: Synthesis and application. *Acc. Chem. Res.* **2002**, 35 (12), 1008–1017.
21. T. Ueda, M.M.H. Bhuiyan, H. Norimatsu, et al. Development of carbon nanotube-based gas sensors for NO_x gas detection working at low temperature. *Phys. E Low-Dimensional Syst. Nanostructures* **2008**, 40 (7), 2272–2277.
22. S. Rathinavel, K. Priyadarshini, D. Panda. A review on carbon nanotube: An overview of synthesis, properties, functionalization, characterization, and the application. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **2021**, 268 (January 2020), 115095.
23. J. Joseph, N. Pradeep, J. Markna, D. Pandya. Fabrication of MWCNTs Based Oxygen Gas Sensor using CCVD technique. *Artic. Int. J. Innov. Res. Sci. Eng. Technol.* **2017**, 3297 (6).
24. G. Verma, K. Mondal, A. Gupta. Si-based MEMS Resonant Sensor : A Review from Microfabrication Perspective. *Microelectronics J.* **2021**, 118, 1–64.
25. C.E. Baddour, C. Briens. Carbon nanotube synthesis: A review. *Int. J. Chem. React. Eng.* **2005**, 3, 1–20.
26. M. Mittal, A. Kumar. Carbon nanotube (CNT) gas sensors for emissions from fossil fuel burning. *Sensors and Actuators, B: Chemical*. Elsevier B.V. 2014, pp 349–362.
27. C. Chen, Y. Zhang. Carbon Nanotube Structure, Electronic, and Transport Properties. *Nanowelded Carbon Nanotub.* **2009**, 1–13.
28. N. Saifuddin, A. Z. Raziah, A. R. Junizah. Carbon Nanotube: A Review on Structure and Their Interaction. *J. Chem.,* **2013**, 2013, 1–18.
29. P. Avouris, Z. Chen, V. Perebeinos. Carbon-based electronics. *Nat. Nanotechnol.* **2007**, 2 (10), 605–615.
30. R.F. Araújo, M.F. Proença, C.J. Silva, et al. Grafting of adipic anhydride to carbon nanotubes through a Diels-Alder cycloaddition/oxidation cascade reaction. *Carbon N. Y.* **2016**, 98, 421–431.
31. F.A. Gutierrez, J.M. Gonzalez-Dominguez, A. Ansón-Casas, et al. Single-walled carbon nanotubes covalently functionalized with cysteine: A new alternative for the highly sensitive and selective Cd(II)

- quantification. *Sensors Actuators, B Chem.* **2017**, 249, 506–514.
32. F. Ernst, Z. Gao, R. Arenal, et al. Noncovalent Stable Functionalization Makes Carbon Nanotubes Hydrophilic and Biocompatible. *J. Phys. Chem. C* **2017**, 121 (34), 18887–18891.
 33. S.K. Misra, P. Moitra, B.S. Chhikara, P. Kondaiah, S. Bhattacharya. Loading of single-walled carbon nanotubes in cationic cholesterol suspensions significantly improves gene transfection efficiency in serum. *J. Mater. Chem.* **2012**, 22 (16), 7985–7998.
 34. B.S. Chhikara, S.K. Misra, S. Bhattacharya. CNT loading into cationic cholesterol suspensions show improved DNA binding and serum stability and ability to internalize into cancer cells. *Nanotechnology* **2012**, 23 (6), 065101.
 35. D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato. Chemistry of Carbon Nanotubes. *Chem. Rev.* **2006**, 106 (3), 1105–1136.
 36. S. Peng, K. Cho. Chemical control of nanotube electronics. *Nanotechnology* **2000**, 11 (2), 57–60.
 37. J.T.W. Yeow, Y. Wang. A review of carbon nanotubes-based gas sensors. *J. Sensors* **2009**, 2009.
 38. X. Zhang, H. Cui, Y. Gui, J. Tang. Mechanism and Application of Carbon Nanotube Sensors in SF₆ Decomposed Production Detection: a Review. *Nanoscale Res. Lett.* **2017**, 12 (1), 177.
 39. L. Heroux, V. Krungleviciute, M.M. Calbi, A.D. Migone. CF₄ on carbon nanotubes: Physisorption on grooves and external surfaces. *J. Phys. Chem. B* **2006**, 110 (25), 12597–12602.
 40. M.M. Calbi, J.L. Riccardo. Energy barriers at the ends of carbon nanotube bundles: Effects on interstitial adsorption kinetics. *Phys. Rev. Lett.* **2005**, 94 (24), 1–4.
 41. D.S. Rawat, M.M. Calbi, A.D. Migone. Equilibration time: Kinetics of gas adsorption on closed- and open-ended single-walled carbon nanotubes. *J. Phys. Chem. C* **2007**, 111 (35), 12980–12986.
 42. K.A. Williams, P.C. Eklund. Monte Carlo simulations of H₂ physisorption in finite-diameter carbon nanotube ropes. *Chem. Phys. Lett.* **2000**, 320 (3–4), 352–358.
 43. K. Xu, X. Tian, C. Wu, et al. Fabrication of single-walled carbon nanotube-based highly sensitive gas sensors. *Sci. China Technol. Sci.* **2013**, 56 (1), 32–35.
 44. E. Dilonardo, M. Penza, M. Alvisi, et al. Electrophoretic deposition of Au NPs on MWCNT-based gas sensor for tailored gas detection with enhanced sensing properties. *Sensors Actuators, B Chem.* **2016**, 223 (2), 417–428.
 45. S. Brahim, S. Colbern, R. Gump, L. Grigorian. Tailoring gas sensing properties of carbon nanotubes. *J. Appl. Phys.* **2008**, 104 (2), 2956395.
 46. H.Y. Jung, S.M. Jung, J. Kim, J.S. Suh. Chemical sensors for sensing gas adsorbed on the inner surface of carbon nanotube channels. *Appl. Phys. Lett.* **2007**, 90 (15), 1–4.
 47. T. Kawano, H.C. Chiamori, M. Suter, et al. An electrothermal carbon nanotube gas sensor. *Nano Lett.* **2007**, 7 (12), 3686–3690.
 48. M. Penza, R. Rossi, M. Alvisi, E. Serra. Metal-modified and vertically aligned carbon nanotube sensors array for landfill gas monitoring applications. *Nanotechnology* **2010**, 21 (10), 105501.
 49. S. Abdulla, T.L. Mathew, B. Pullithadathil. Highly sensitive, room temperature gas sensor based on polyaniline-multiwalled carbon nanotubes (PANI/MWCNTs) nanocomposite for trace-level ammonia detection. *Sensors Actuators, B Chem.* **2015**, 221, 1523–1534.
 50. S.J. Young, Z.D. Lin. Ethanol gas sensors based on multi-wall carbon nanotubes on oxidized Si substrate. *Microsyst. Technol.* **2018**, 24 (1), 55–58.
 51. C. Zhou, J. Zhao, J. Ye, et al. Printed thin-film transistors and NO₂ gas sensors based on sorted semiconducting carbon nanotubes by isoindigo-based copolymer. *Carbon N. Y.* **2016**, 108 (2), 372–380.
 52. M. Ghanbarian, S. Zeinali, A. Mostafavi. A novel MIL-53(Cr-Fe)/Ag/CNT nanocomposite based resistive sensor for sensing of volatile organic compounds. *Sensors Actuators, B Chem.* **2018**, 267, 381–391.
 53. D. Maity, K. Rajavel, R.T.R. Kumar. Polyvinyl alcohol wrapped multiwall carbon nanotube (MWCNTs) network on fabrics for wearable room temperature ethanol sensor. *Sensors Actuators, B Chem.* **2018**, 261, 297–306.
 54. R. Guo, H. Wang, R. Tian, et al. The enhanced ethanol sensing properties of CNT @ ZnSnO₃ hollow boxes derived from Zn-MOF (ZIF-8). *Ceram. Int.* **2020**, 46 (6), 7065–7073.
 55. L. Sacco, S. Forel, I. Florea, C.S. Cojocaru. Ultra-sensitive NO₂ gas sensors based on single-wall carbon nanotube field effect transistors: Monitoring from ppm to ppb level. *Carbon N. Y.* **2020**, 157 (2), 631–639.
 56. A. Sachan, M. Castro, V. Choudhary, J.-F. Feller. vQRS Based on Hybrids of CNT with PMMA-POSS and PS-POSS Copolymers to Reach the Sub-PPM Detection of Ammonia and Formaldehyde at Room Temperature Despite Moisture. *Chemosensors* **2017**, 5 (3), 22.
 57. B. Kumar, Y.T. Park, M. Castro, J.C. Grunlan, J.F. Feller. Fine control of carbon nanotubes-polyelectrolyte sensors sensitivity by electrostatic layer by layer assembly (eLbL) for the detection of volatile organic compounds (VOC). *Talanta* **2012**, 88, 396–402.
 58. M. Shooshitari, A. Salehi, S. Vollebregt. Effect of Humidity on Gas Sensing Performance of Carbon Nanotube Gas Sensors Operated at Room Temperature. *IEEE Sens. J.* **2021**, 21 (5), 5763–5770.
 59. Z. Gao, Z. Lou, S. Chen, et al. Fiber gas sensor-integrated smart face mask for room-temperature distinguishing of target gases. *Nano Res.* **2018**, 11 (1), 511–519.
 60. W. Zhang, S. Cao, Z. Wu, et al. High-Performance Gas Sensor of Polyaniline/Carbon Nanotube Composites Promoted by Interface Engineering. *Sensors* **2019**, 20 (1), 149.
 61. A. Safavi, N. Maleki, M.M. Doroodmand. Fabrication of a room temperature hydrogen sensor based on thin film of single-walled carbon nanotubes doped with palladium nanoparticles. *J. Exp. Nanosci.* **2013**, 8 (5), 717–730.
 62. Z.H. Khan, M.S. Ansari, N.A. Salah, A. Memic, S. Habib. Cobalt catalyzed multi walled carbon nanotubes film sensor for carbon monoxide gas. *Dig. J. Nanomater. Biostructures* **2011**, 6 (4), 1947–1956.
 63. J. Sippel-Oakley, H.T. Wang, B.S. Kang, et al. Carbon nanotube films for room temperature hydrogen sensing. *Nanotechnology* **2005**, 16 (10), 2218–2221.
 64. S. Kumar, V. Pavelyev, P. Mishra, N. Tripathi. Sensitive detection of Nitrogen Dioxide using gold nanoparticles decorated Single Walled Carbon Nanotubes. *Int. Conf. "Information Technol. Nanotechnol.* **2017**, 74–77.
 65. C. Piloto, F. Mirri, E.A. Bengio, et al. Room temperature gas sensing properties of ultrathin carbon nanotube films by surfactant-free dip coating. *Sensors Actuators, B Chem.* **2016**, 227, 128–134.
 66. I. Sasaki, N. Minami, A. Karthigeyan, K. Iakoubovskii. Optimization and evaluation of networked single-wall carbon nanotubes as a NO₂ gas sensing material. *Analyst* **2009**, 134 (2), 325–330.
 67. S. Gaikwad, G. Bodkhe, M. Deshmukh, et al. Chemiresistive sensor based on polythiophene-modified single-walled carbon nanotubes for

- detection of NO₂. *Modern Physics Lett. B*, **2015**, 29, 1–5.
68. L. Vatandoust, A. Habibi, H. Naghshara, S.M. Aref. Fabrication of ZnO-MWCNT nanocomposite sensor and investigation of its ammonia gas sensing properties at room temperature. *Synthetic Metals*, **2021**, 273, 116710.
 69. S. Manivannan, L.R. Shobin, A.M. Saranya, et al. Carbon nanotubes coated fiber optic ammonia gas sensor. *Integr. Opt. Devices, Mater. Technol. XV* **2011**, 7941, 79410M.
 70. L.Q. Nguyen, P.Q. Phan, H.N. Duong, C.D. Nguyen, L.H. Nguyen. Enhancement of NH₃ gas sensitivity at room temperature by carbon nanotube-based sensor coated with Co nanoparticles. *Sensors (Switzerland)* **2013**, 13 (2), 1754–1762.
 71. M. Sinha, S. Neogi, R. Mahapatra, S. Krishnamurthy, R. Ghosh. Material dependent and temperature driven adsorption switching (p- to n- type) using CNT/ZnO composite-based chemiresistive methanol gas sensor. *Sensors Actuators, B Chem.* **2021**, 336 (February), 129729.
 72. H.T. Hussein, M.H. Kareem, A.M. Abdul Hussein. Synthesis and characterization of carbon nanotube doped with zinc oxide nanoparticles CNTs-ZnO/PS as ethanol gas sensor. *Optik (Stuttg.)*. **2021**, 248 (September), 168107.
 73. S.M. Iordache, E.I. Ionete, A.M. Iordache, et al. Pd-decorated CNT as sensitive material for applications in hydrogen isotopes sensing - Application as gas sensor. *Int. J. Hydrogen Energy* **2021**, 46 (18), 11015–11024.
 74. Z. Ahmad, Naseem, S. Manzoor, et al. Self-standing MWCNTs based gas sensor for detection of environmental limit of CO₂. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **2020**, 255 (Jan), 114528.
 75. S.-J. Young, Z.-D. Lin. Sensing Performance of Carbon Dioxide Gas Sensors with Carbon Nanotubes on Plastic Substrate. *ECS J. Solid State Sci. Technol.* **2017**, 6 (5), M72–M74.
 76. N. Kohli, A. Hastir, M. Kumari, R.C. Singh. Hydrothermally synthesized heterostructures of In₂O₃/MWCNT as acetone gas sensor. *Sensors Actuators, A Phys.* **2020**, 314, 112240.
 77. Q. Tan, J. Fang, W. Liu, J. Xiong, W. Zhang. Acetone sensing properties of a gas sensor composed of carbon nanotubes doped with iron oxide nanopowder. *Sensors (Switzerland)* **2015**, 15 (11), 28502–28512.
 78. S. Salehi, E. Nikan, A.A. Khodadadi, Y. Mortazavi. Highly sensitive carbon nanotubes-SnO₂ nanocomposite sensor for acetone detection in diabetes mellitus breath. *Sensors Actuators, B Chem.* **2014**, 205, 261–267.
 79. Y. Seekaew, A. Wisitsoraat, D. Phokharatkul, C. Wongchoosuk. Room temperature toluene gas sensor based on TiO₂ nanoparticles decorated 3D graphene-carbon nanotube nanostructures. *Sensors Actuators, B Chem.* **2019**, 279 (September 2018), 69–78.

AUTHORS BIOGRAPHIES



field of flexible gas sensing devices.

Gulshan Verma is currently a Ph.D. scholar in the Department of Mechanical Engineering at the Indian Institute of Technology Jodhpur, India. His area of interest includes MEMS systems, nanocomposites-based sensors, and flexible sensors. His current research focuses on the



Dr. Ankur Gupta is an Assistant Professor in the Department of Mechanical Engineering at the Indian Institute of Technology Jodhpur, India. His research interest lies in Microsystem design and manufacturing.