#### **REVIEW**



# **A review of gas sensors based on carbon nanomaterial**

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#### **Abstract**

As a new nanostructure, a graphene is a compound of carbon atoms with a two-dimensional structure that has attracted the attention of many nanoscale researchers due to its novel physical and chemical properties. The presence of all graphene atoms in the surface and its unique electrical properties, as well as the ability to functionalize and combine with another nanomaterial, has introduced graphene as a new and suitable candidate material for gas sensing. Over the years, many researchers have turned their attention to carbon nanomaterial. The unique optical, mechanical, and electronic properties of these nanostructures have led them to use these nanomaterials to develop tiny devices, such as low-consumption sensors. Carbon nanomaterial poses a threat to another nanomaterial in terms of their use in gas sensors. This review article discusses the use of carbon nanoparticles and graphene in gas sensors, examines the nodes in the commercialization pathway of these compounds, and presents the latest achievements. Finally, the perspectives of the challenges and opportunities in the feld of sensors based on carbon nanomaterial and graphene are examined.

**Keywords** Graphene · Nanomaterial · Two-dimensional · Sensors · Carbon nanomaterial · Electronic

# **1 Introduction**

Sensors today are of undeniable importance in industry and research that is can perform detection by quantifying a physical or chemical phenomenon at the sensor surface and converting changes into an electrical, mechanical, or optical signal  $[1-4]$  $[1-4]$ . Today, due to the undeniable applications of gases

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in industry, agriculture, homes, research, and even outside the atmosphere in the feld of space science, detecting and measuring the type and concentration of gases, especially toxic and fammable gases, is inevitable [\[5](#page-18-2)–[9\]](#page-18-3). Therefore, the necessity of introducing and manufacturing new sensors from sensitive materials with appropriate selectivity is determined [\[10,](#page-18-4) [11](#page-18-5)]. The feld of nanotechnology, with its large number and variety of nanomaterial with high volume, modifability, and engineering of physical and chemical properties of their surface, introduces many candidates for gas sensing [\[12](#page-18-6)]. The dramatic use of nanoparticles, nanowires, and nanotubes as gas sensors and chemical evidence for this claim [[13–](#page-18-7)[18\]](#page-19-0). These new nanostructures, with high efective surface area and improved sensor parameters can be a good alternative to the old sensors, are often based on mineral semiconductors and metal oxides [[19,](#page-19-1) [20](#page-19-2)]. One of these emerging nanoparticles is graphene as a compound of carbon atoms with hexagonal lattices, which since its discovery in 2004 has attracted the attention of many researchers in various felds—such as Nano electronics, nanophysics, Nano chemistry, nanomaterial, nanoparticles, etc. [\[21](#page-19-3)[–25](#page-19-4)]. Placement of all grapheme atoms on the surface, interesting electrical, mechanical and chemical properties, and a variety of manufacturing methods are some of the reasons

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that can make graphene a good candidate for sensing [\[26,](#page-19-5) [27](#page-19-6)]. Although graphene itself is a gas-absorbing material, it can achieve better sensitivity and selectivity for gas sensing in hybrid structures with another nanomaterial by taking advantage of the synergistic efect to improve sensitivity and selectivity. one of the limitations of graphene as a gas sensor sensitivity is not so high in the presence of environmental contamination—because of the nature of Lipophilicity, low selectivity, and desorption of the absorbed species problem to return the sensor to initial conditions—he said. Therefore, selecting, designing, and manufacturing new graphene-based hybrid compounds with another nanomaterial is one of the major challenges in this area [\[28–](#page-19-7)[31](#page-19-8)]. Over the past few years, the number of articles on nanomaterial gas sensors has increased dramatically. In today's world, electronic sensors strongly need a stable, sensitive, and simple that minimal quantities of gases step, routers choose, it is felt. Such sensors can be used to detect biomass or hazardous chemical agents. At present, the construction of such sensors is costly due to the complexity of materials and equipment, therefore there is a great deal of focus on making cheaper and more efficient sensors  $[32-35]$  $[32-35]$  $[32-35]$ . Of all the nanomaterial, a carbon nanomaterial is a great option for this. Carbon nanomaterial has a high potential for automated sensors due to their inherent properties. Low-dimensional carbon structures have a high surface area that is ideal for sensing [\[36–](#page-19-11)[38](#page-19-12)]. Unlike polycrystalline materials such as metal oxides, quasi-dimensional carbon materials have no grain boundaries, making the sensor long-term stable. Some carbon materials, such as carbon nanotubes and graphene, have high-quality crystal lattices, so load carriers in these structures move at high speeds while generating little noise [\[39–](#page-19-13)[42\]](#page-19-14). Since these two factors play a critical role in creating conductivity properties, it is easier to control and understand the surface chemistry of low-dimensional materials and high-quality crystal structures. Single crystal nanostructures are a great option for studying computational chemistry [\[43–](#page-19-15)[45](#page-19-16)]. The sensitivity and selectivity of carbon materials can be manipulated by various methods, for example, structural defects and the creation of functional groups at the surface of nanotubes can be used for this purpose [[46](#page-19-17)[–48\]](#page-19-18). The Carbon nanotubes can be used to build various implements used in various ways. Low-cost methods such as lithography are suitable for making these devices. The mechanical properties of carbon nanotubes allow them to be used in fexible electronic devices [[49](#page-19-19), [50\]](#page-19-20). Another advantage of carbon nanotubes is the high cost-sensitivity ratio, which is high even at room temperature [[51–](#page-19-21)[53](#page-19-22)]. The low energy consumption of carbon nanotube-based devices allows them to operate independently and without the need for an external charger [\[54](#page-19-23)]. The movement of electronic signals in a chemical environment has advantages over optical methods; For example, the cost of these methods is low and their output is high, and in addition to simplicity, they are portable [[55,](#page-19-24) [56](#page-20-0)]. Fullerenes are compounds with unparalleled electrical conductivity, high tensile strength, optical and thermal properties. The antimicrobial properties of fullerenes are among the recent fndings of researchers. Fullerenes are almost insoluble in water. However, some soluble derivatives of fullerenes have signifcant antimicrobial efects. Fullerenes can form stable nanoparticle suspensions called nc60, which have stronger antimicrobial efects. Polyhydroxylated fullerenes [C60(OH)*n*], known as fullerenes, have stronger antimicrobial activity and less toxicity than nc60 [[57–](#page-20-1)[60\]](#page-20-2).

In this review article, the use of carbon materials in the to construct various high-performance gas sensors is discussed, and its strengths and weaknesses are evaluated.

## **2 Carbon nanomaterial**

Over the past few years, much research has been done on the use of carbon nanomaterial in the manufacture of sensors. More recently, graphene, as one of the new carbon allotropes, is overtaking carbon nanotubes in sensor construction [\[61](#page-20-3)[–65](#page-20-4)]. But carbon nanomaterial is not limited to graphene and nanotubes, so structures such as nanoparticles, nanofbers, and Nano porous carbon materials can also be classifed in this section. One of the most important reasons for the interest in making sensors from carbon nanomaterial is that these materials, in addition to having a regular nanoscale tubular structure, also have considerable stability; so they are very stable even when they are not functional [[66–](#page-20-5)[68\]](#page-20-6). Although there are a wide range of nanomaterial, their reactive chemistry is similar: organic chemistry. Before examining the use of carbon nanomaterial in electric gas sensors, we will briefy discuss the properties and production methods of some of these nanomaterial [[69](#page-20-7)[–71](#page-20-8)]. Figure [1](#page-1-0) shows Schematic illustration of individual allotropes of Carbon nanotubes.

# **2.1 Carbon black**

Black carbon is pure carbon within the sort of colloidal particles produced by the strategy of incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions [\[72–](#page-20-9)[75\]](#page-20-10). The physical

<span id="page-1-0"></span>

**Fig. 1** Schematic illustration of individual allotropes of carbon nanomaterial [\[1](#page-18-0)–[5\]](#page-18-2)

appearance of this substance is black and it exists within the variety of powder or granules. Most carbon within the world is produced by both furnace and warmth methods, of which furnace carbon is that the most typical. During this method, very heavy aromatic oils are used as staple [\[76–](#page-20-11)[78](#page-20-12)]. Under controlled conditions, the oil is heated in a very furnace and atomic number 6 is produced at specifc pressures and temperatures. To do this, the oil evaporates and after pyrolysis turns into carbon micro particles. In most furnace reactors, the reaction rate is controlled by the flow of water or vapor  $[79-82]$  $[79-82]$  $[79-82]$ . The produced carbon is taken out of the reactor and cooled, and eventually packed after passing through a flter. Various gases, like CO and hydrogen, remain within the process. Most soot factories use a number of these residual gases to get heat, steam, or electricity [[83](#page-20-15)[–86\]](#page-20-16). Within the heating method, gas is employed to provide soot, and compounds like heavy aromatic oils or methane are used because the primary feed of this method. During this method, two separate furnaces are usually accustomed produce  $C$ , so the stuff enters the second furnace (carbon black production) 5 min after leaving the primary furnace (initial heating) [\[87–](#page-20-17)[93\]](#page-21-0). Fossil fuel is injected into a hot furnace and within the absence of air, the oil decomposes to C. Aerosols produced by the flow of vapor were taken out of the system and trapped within the filters [[94–](#page-21-1)[96](#page-21-2)]. Various processes could also be accustomed purify and separate the unwanted compounds during this method so the output product is packaged. The hydrogen produced by this method will be wont to heat the second furnace. smut is physically and chemically quite distinct from soot, a substance during which quite 97% of its structure is clustered. Carbon encompasses a high extent, in order that its area is quite thousand  $g/cm<sup>3</sup>$  and its cavity dimensions are but 50 nm [\[97–](#page-21-3)[100](#page-21-4)]. The density of lampblack is way under the theoretical density of graphite  $(2.25 \text{ g/cm}^3)$  $(2.25 \text{ g/cm}^3)$  $(2.25 \text{ g/cm}^3)$ . Figure 2 shows a high resolution image of a transmission microscope (TEM).

#### **2.2 Carbon nanofbers**

Vapor phase-grown carbon nanofbers (VGCNF) are carbon nanoscale fbers that are formed from hydrocarbon gases on metal catalysts such as nickel, iron, and cobalt at high temperatures (900–1500 °C) [\[101–](#page-21-5)[105\]](#page-21-6). These hollow fibers are tubular in shape and grow from a primary graphite core 20–60 nm in diameter on the surface of the catalyst. The thickness of these nanofbers can be increased by using additional layers created by CVD method [\[106](#page-21-7)[–112\]](#page-21-8). Subsequent layers are added to  $SP<sup>3</sup>$  hybridizing carbon on the nanofiber wall. The diameter of these nanofbers varies from 60–70 nm to 200 nm and their length can be from 1 to 100 nm [\[107,](#page-21-9) [108,](#page-21-10) [110,](#page-21-11) [111](#page-21-12), [113,](#page-21-13) [114](#page-21-14)]. On the other hand, carbon nanofbers can be obtained in various controlled conditions with low cost and high growth rate using electro spinning method. A polymer such as polyacrylate (PAN) is used as the carbon source [[115,](#page-21-15) [116](#page-21-16)]. This polymer is combined with suitable solvents and heated to a temperature below the boiling point and then used as a polymer solution in the electro spinning process. This solution is injected into a rotating tube using a special syringe. Voltage is applied between the syringe and the tube, which are a few centimeters apart [[117](#page-21-17)[–121](#page-21-18)]. The produced material is heat treated for several hours at a temperature of 300–400 °C. The product is then calcined and carbonized in the absence of oxygen (in an argon or nitrogen atmosphere) at 700–1000 °C [[122–](#page-21-19)[126](#page-21-20)]. The final product will be carbon nanofibers with a diameter of 40–400 nm and a length of over 70 microns (Fig. [3\)](#page-3-0).

#### **2.3 Carbon nanotube**

There are diferent carbon allotropes; the carbon atoms in diamond have a tetrahedral lattice arrangement. In graphite, the carbon atoms are in the form of hexagonal sheets, and in graphene and fullerene, the atoms are arranged in a spherical or tubular manner [[127](#page-21-21)[–130](#page-22-0)]. Carbon nanotubes

<span id="page-2-0"></span>**Fig. 2** Transmission electron microscope photos showing a high (**A**) and low (**B**) degree of accumulation in various carbon blacks [[2\]](#page-18-8)



<span id="page-3-0"></span>



have a fullerene-like structure that can be closed at the end [[131](#page-22-1)[–135\]](#page-22-2). The name of these nanostructures is derived from their physical shape in which graphene tubular sheets with diferent tubing angles lead to tubes with diferent symmetries [\[136](#page-22-3), [137\]](#page-22-4). The angle of tubing and the radius of the tube determine the appearance of metal or semiconductor properties in these nanostructures. Nanotubes are divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [\[138](#page-22-5)[–141\]](#page-22-6). In multiwalled nanotubes, several graphene sheets are tubed. Carbon nanotubes naturally adhere to each other due to the van der Waals effect. These nanotubes are bonded together using a  $Sp<sup>2</sup>$  bond, similar to the interaction between graphite layers. The  $Sp<sup>2</sup>$  bond is stronger than the  $Sp<sup>3</sup>$  bond and is a bond between alkanes and diamonds, resulting in the unique structural strength of the nanotubes. Such strong bonds reduce the activity of nanotubes with surrounding molecules. Therefore, functionalization of carbon nanotubes is a suitable tool to improve the sensitivity and selectivity of nanotubes in the construction of gas sensors. Carbon nanotubes are produced using various methods, such as CVD, laser irradiation and discharge. Carbon nanotubes were frst seen in 1991 among graphene soot products from discharge. In this process, the carbon in the negative electrode is sublimated due to the high temperature in the discharge process [\[142](#page-22-7)[–144\]](#page-22-8). Since this method was frst used to synthesize nanotubes, it is known as the most common method of producing carbon nanotubes. In this method, the yield of the product has been 30% by weight, which includes both types of nanotubes, single-walled and multi-walled, with lengths of up to 50 microns containing structural defects. In the laser irradiation process, a laser is used to evaporate graphite and an inert gas is used to conduct these vapors into the tank. Carbon nanotubes grow on the cold surface of the reactor. This method, developed by Smiley et al., Is suitable for the production of multi-walled carbon nanotubes [\[142–](#page-22-7)[149](#page-22-9)]. The team used graphite composite and metal catalyst particles (a combination of cobalt and nickel) to synthesize single-walled carbon nanotubes. The efficiency of this process is  $70\%$  and its main

product is single-walled carbon nanotubes. The diameter of these nanotubes is completely controllable and the diameter of the nanotubes can be controlled as desired by changing the temperature  $[150-153]$  $[150-153]$  $[150-153]$ . A research team used the catalyst-assisted CVD method to produce carbon nanotubes. During the CVD process, a layer of metal catalyst particles, generally nickel, cobalt, and iron, was used to produce carbon nanotubes [[58–](#page-20-18)[60](#page-20-2)]. CVD is a common method for the commercial production of carbon nanotubes [[58](#page-20-18)[–156](#page-22-12)]. In this method, the diameter of the nanotubes is related to the dimensions of the metal particles. The diameter of the nanotubes can be controlled by substrate patterning, heat treatment and plasma catalyst etching. In this method, gases such as nitrogen, hydrogen and ammonia are injected into the tank and the temperature reaches 700 degrees, then carbon-containing gases such as acetylene, ethylene, ethanol and methane are blown into the tank [\[157](#page-22-13), [158\]](#page-22-14). These gases are broken down by heat, and the carbon atoms attach to the edge of the catalyst metal particles, and the growth of carbon nanotubes begins. Catalyst particles can stick to the tip of nanotubes and stick with them, depending on the type of catalyst used. If a strong electric feld is used to grow carbon nanotubes, the nanotubes will grow in the direction of the applied feld [\[158–](#page-22-14)[161\]](#page-22-15). By adjusting the geometric shape of the reactor, the nanotubes can be grown vertically (so that they grow perpendicular to the substrate). Without feld application, the growth of nanotubes occurs randomly in different directions. However, under certain conditions, nanotubes can be grown as dense, high-density vertical arrays to achieve a forest-like or carpet-like structure [[162](#page-22-16)[–164,](#page-23-0) [235](#page-25-0)[–239](#page-25-1)]. Among the various methods of producing carbon nanotubes discussed in this article, laser irradiation is the most expensive and the least efficient method of producing carbon nanotubes. Therefore, the CVD method is the best option for the industrial production of carbon nanotubes [[165–](#page-23-1)[168,](#page-23-2) [240–](#page-25-2)[242](#page-25-3)]. The reason for this is the low cost-to-income ratio, as well as the possibility of vertical growth of nanotubes on the desired substrate. Carbon nanotube growth sites must be carefully placed on the surface.

Figure [4](#page-4-0) shows a picture of multi-walled carbon nanotubes grown to 50 microns by CVD with 95% purity. The thickness of the outer and inner layers of these nanotubes is 3–15 and 3–7 nm, respectively. In this image, the nanotubes are randomly oriented to create a porous material-like structure. Figure [4](#page-4-0) shows Schematic structure and TEM images of single-walled carbon nanotubes and Multi-Walled Carbon Nanotubes [[67–](#page-20-19)[69](#page-20-7)].

## **2.4 Graphene**

Kostya Novoselov et al. [[81,](#page-20-20) [82](#page-20-14)] showed that the material had interesting electrical properties. Graphene has a high electrical conductivity due to its quality crystal structure. Electrical gap band, type of charge carriers and density of charge carriers can be changed in graphene; this can be done by applying diferent gate voltages to the substrate. Some of the properties of graphene make it a good choice for building a gas sensor  $[169-172]$  $[169-172]$  $[169-172]$ . Because graphene is two-dimensional and the entire surface of the material is in contact with the environment, graphene has the highest surface area per unit volume. The high conductivity of this material causes its conductivity to be similar to that of metals, and its Johnson noise is very low, while the presence of a few extra electrons changes the concentration of charge carriers [\[173–](#page-23-5)[176\]](#page-23-6). This grapheme can be transferred to other substrates. The main challenge of growing graphene in CVD is that it is not possible to precisely control the number of layers grown, and also metal contaminants originating from the metal substrate enter the product. Figure [5](#page-4-1) is a graphene micrograph taken using a modifed TEM image.

# **2.5 Magnetron sputtering method of C‑based nanostructured materials**

Magnetron sputtering catholic sputtering of target material in magnetron discharge plasma allows obtaining thin flms and coatings on various supports. Dutch physicist F. Penning was the primary to suggest using magnetron sputtering for the flm deposition as early as 1935. Material sputtering in magnetron discharge was studied in several laboratories within the 1960s and within the 1970s various configurations of magnetron sputtering systems (MSS), including prototypes of recent planar magnetrons, were proposed. Industrial application of this technology started at the tip of the 1970s. Since then high-power impulse systems are designed additionally to DC and RF classical variants. Development of recent magnetrons is continuous now. Method of catalytic layers' deposition by magnetron sputtering has been developed and surface Raney catalysts and new efective catalysts for various processes are synthesized. Development of those works resulted within the creation of catalytic



<span id="page-4-1"></span><span id="page-4-0"></span>**Fig. 4** Schematic structure and TEM images of single-walled carbon nanotubes and multi-walled carbon nanotubes. **A** Schematic structure of single-walled carbon nanotubes and **b** multi-walled carbon nanotubes. The transmission electron microscope (TEM) images of a **C** single-walled carbon nanotubes and **d** multi-walled carbon nanotubes [[42](#page-19-14)] **Fig. 5** Micrograph of graphene atomic structure [\[31,](#page-19-8) [32\]](#page-19-9)



membrane reactors [[177–](#page-23-7)[179](#page-23-8)]. Carbon supports were considered closely: coating deposition added catalytic properties and improved thermal and chemical stability. Solving some problems important for hydrogen energy development (e.g. encapsulation of hydride forming powders, synthesis of catalysts on granules) needs various flms/coatings (including Pt, Pd ones) on disperse carriers. Shortly new devices for prevention of powder aggregation were designed. Preliminary experiments on deposition of Cu and Ni on carbon powders showed the likelihood of carbon nanomaterials and carbon based nanocomposites coating [[155\]](#page-22-17).

# **3 Gas sensors with carbon nanomaterial**

Various properties of carbon nanomaterial, such as optical and electrical properties, have led to the use of these materials to build sensors [\[180–](#page-23-9)[182\]](#page-23-10). The diferent properties of graphene in a liquid medium, including pH sensors, heavy ions, have led to the use of these materials to make sensors. This review article is limited to the construction of gas sensors that change the electric current passing through them due to the target material [[183,](#page-23-11) [184\]](#page-23-12).

#### **3.1 Carbon‑black gas sensors**

In these sensors, the carbon block is dispersed inside an insulating polymer, providing electrical conductivity to the flm. If the desired gas/vapor is present, the polymer swells and eventually the electrical conductivity/resistance of the polymer changes. Using a suitable solvent, the viscosity of the polymer/carbon block is adjusted optimally, and then the polymer is patterned on the surface of the flter electrode. Various methods are applied to place the polymer on the surface of the electrodes, such as spin coating and droplets, and fnally the coating dries. Changes in the strength of a composite in terms of carbon block percentage are explained using the theory of percolation (penetration) [[185](#page-23-13), [186\]](#page-23-14). If the amount of carbon black is low, the composite will be insulated due to the lack of connection between the conductive particles in the composite body. As the amount of carbon block in the polymer increases, the electrical resistance of the polymer decreases exponentially [\[74–](#page-20-21)[77\]](#page-20-22). By increasing the concentration of carbon block and reaching the transfer point, the connection is established based on the penetration limit. If the desired vapor/gas is present, the polymer swells and the amount of electrical conductivity/resistance changes, this change is used to identify the gas. This mechanism is shown in Fig. [6.](#page-5-0) Lewis and colleagues used arrays of elements to respond to diferent vapors. The team used diferent polymer/carbon black composites to do this.



<span id="page-5-0"></span>**Fig. 6** Gas sensing mechanism of polymer/carbon black composite. Carbon black is dispersed in the polymer matrix. White line that the image above shows the conduction path between the electrodes gives. In the presence of vapors, this path is changed and the direction changes. If vapors are removed from the environment the steering wheel returns to its original position [\[33,](#page-19-25) [37\]](#page-19-26)

Electrical resistance signals are output from these arrays and evaluated using a standard system [[187](#page-23-15)[–189](#page-23-16)]. The aim is to detect the presence of various vapors from organic solvents. This strategy can be combined with various software and hardware systems, and fnally provide a small and compact tool with low cost and ease of use. For example, the sensory responses in the detection of benzene and methanol are shown in Fig. [7.](#page-6-0) In the presence of high concentrations of these toxic fumes, the responses obtained will be moderate. Polymer/carbon composite sensors may be delayed in responding to external stimuli due to aging of the polymer matrix or displacement of carbon black particles. Particle displacement or matrix aging causes a diffusion path [\[78–](#page-20-12)[80\]](#page-20-23). This change in arrangement occurs as a result of repeated swelling and shrinkage of the polymer matrix due to repeated use of the sensor.



<span id="page-6-0"></span>**Fig. 7** Resistance of carbon black composite to **a** polyethylene-covinyl Acetate (**b**) poly (N-vinylpyrrolidone) in the presence of benzene and methanol. These compounds are alternately reduced and increased to repeatability and stability Examined [[38](#page-19-12)]

#### **3.2 Carbon nanofber‑based gas sensors**

To overcome the instability problem of polymer/carbon black composites, Fu et al. [\[40](#page-19-27)] proposed the use of carbon nanofbers in polymers. As the polymer matrix absorbs the vapor, the viscosity of the matrix decreases and its volume increases. Under these conditions, carbon black nanoparticles accumulate in the polymer matrix. However, with the addition of polymer nanofbers, the vapor sensitivity in the polymer is improved and if vapor is adsorbed and desorbed from the composite, the nanofbers are resistant to displacement within the polymer due to their high surface-to-height ratio [\[190](#page-23-17)–[193\]](#page-23-18). As a result, the main electrical penetration path in these composites is maintained after vapor absorption. A research team dispersed carbon nanofbers grown from the vapor phase into toluene and added it to polystyrene. This was done under mechanical rotation conditions. Figure [8](#page-7-0) shows the SEM micrograph in composite films. The response and return cycle for tetrahydrofuran vapors can also be seen in this image.

Lee et al. [[41\]](#page-19-28) proposed an electro spinning method for fabricating polyacrylonitrile/carbon black complexes for use in gas sensors. This method is easily generalizable for mass production and inexpensive. Electro spinning fbers are exposed to heat treatment to form carbon fbers. These fbers are chemically activated to obtain active sites for gas absorption. KOH solution is used as an activating agent,

which improves the structure and increases the specific surface area of carbon fber by almost 100 equal. As a result, the amount of gas absorbed increases dramatically. The surface of the sample is also modifed using fuoridation operations. The applied functional groups increase the gas absorption to the sensor surface. Adding some carbon black also improves electrical conductivity. In total, chemical activation, the presence of carbon black and fuoridation operations improves the sensor response to nitrous oxide and carbon monoxide by up to 5 equal.

Fong et al. [[42\]](#page-19-14) proposed a method for producing carbon nanofbers adorned with Pd nanoparticles that used electro spinning to produce fbers and more chemically to functionalize. These materials are completely uniform and the product of this process is carbon nanofbers with a diameter of 300 nm on which Pd nanoparticles are spread. The dimensions of Pd nanoparticles will be from a few nanometers to a few tens of nanometers.

Surface functionalization is achieved by immersing electro spun polyacrylonitrile fibers in aqueous NH<sub>2</sub>OH solution. The functionalized surface is immersed in Pd  $(NO<sub>3</sub>)<sub>2</sub>$  solution so that the amid oxime functional groups can absorb  $Pd_2$  + ions. The compound is immersed in NH<sub>2</sub>OH solution to allow Pd nanoparticles to adhere to the surface. In the next step, the polymer surface is heat treated to carbonize and stabilize. The same method can be used to produce carbon nanofbers decorated with diferent metal nanoparticles. Electro spun nanofbers are completely fexible and do not change when exposed to hydrogen at room temperature [\[194,](#page-23-19) [195](#page-23-20)]. Sensors made with this method have a good response in a hydrogen-containing environment and the speed of response and return to the original state is acceptable in them. The activity of the sensor surface is highly dependent on the dimensions of the metal clusters attached to the fber surface, and this method can lead to the proper distribution of Pd clusters on the fber surface [[196\]](#page-24-0).

Jang et al. [[43](#page-19-15)] proposed a method for producing electro spun carbon nanofbers decorated with metal oxides. The advantage of this method is that the nanofbers are coated with metal oxide by an extractable method. To create metal oxides ( $ZnO$  and  $SnO<sub>2</sub>$ ) on the surface of carbon fibers, nanofbers with shell core structure (PAN) (PVP) were produced as the starting material. To create these structures, two injection needles should be used in electro spinning; the reason for this is the incompatibility of the two polymers. The root of the incompatibility of the two polymers is the diference in the inherent physical properties of the polymers, especially their viscosity. By decomposing the PVP phase, very small hybrids of CNFs are created, which eventually lead to the conversion of metal precursors  $(ZnAc<sub>2</sub>)$ and  $SnCl<sub>4</sub>$ ) to metal oxide nanostructures. Also, during the heat treatment process, PANs are converted to 40 nm CNFs. The morphology of metal nanostructures can be controlled <span id="page-7-0"></span>**Fig. 8** Micrograph of carbon nanofbers grown to form gives a polystyrene composite. Percentage of nanofbers 25.6 Percentage by weight [upper left (and 5.12% by weight) high right Is. The arrow indicates the point of contact between the fbers Creates a bridge in this network. Electrical response Composite 25.6% by weight at 35 °C In the presence of water vapor and tetrahydrofuran vapor is seen [[40](#page-19-27)]



by varying the concentration of the precursor in the PVP solution. Nanofibers coated with metal oxide are introduced into the ethanol solution and exposed to ultrasonic; then, using the spin coating method, it is placed on the electrode arrays to measure their conductivity. These sensors were tested in the presence of dimethyl methyl phosphonate (DMMP) at room temperature. The minimum detection level of hybrid carbon nanofbers is 0.1 parts per million (ppm). This high sensitivity is due to the presence of metal oxide nanostructures on the surface of carbon nanofbers, which increases the surface area and the tendency of DMMP to vapors. However, the efect of ambient humidity on the responses in this sensor has not yet been discussed. Figure [9](#page-8-0) shows SEM images with high and low resolution of carbon nanofbers decorated with various metal oxides. The normalized response to diferent concentrations in air is also shown.

#### **3.3 Carbon nanotube‑based gas sensors**

The electronic properties of carbon nanotubes are highly sensitive to the chemical environment around the nanotubes. This sensitivity is a suitable tool for using nanotubes in the sensor sector.

Dai et al. [\[44\]](#page-19-29) produced semiconductor single-walled carbon nanotubes using the CVD growth method on a  $SiO<sub>2</sub>/Si$  substrate. By connecting a wire to the nanotubes and creating a metal/nanotube/metal structure, the team was able to build a transistor that could change direction due to diferent voltages. The electrical conductivity of these nanotubes was investigated in the presence of ammonium vapors and nitrogen dioxide [[197–](#page-24-1)[199](#page-24-2)]. The singlewalled carbon nanotube used in this study was a cavityreinforced semiconductor. The results showed that due to

<span id="page-8-0"></span>**Fig. 9** High image: FESEM images with high resolution power from  $SnCl<sub>4</sub>$  in PVP solution ZnAc2 and Carbon nanofbers in the presence Concentrations **a** 0.5, **b** 0.75, **c** 1, **d** 1.25, **e** 1.5 and **f** 2 Weight percent is showing. The image below shows the normalized resistance changes in Indicates the presence of DMMP vapors [[43](#page-19-15)]

![](_page_8_Figure_3.jpeg)

the application of positive gate voltage to this system, the electrical conductivity is reduced three times. Figure [10](#page-9-0) shows the electrical response of the single-walled carbon nanotube device to gaseous molecules. In the presence of ammonia gas, the nanotube capacity band moves away from the Fermi surface, which reduces the number of cavities and thus the conductivity. In the case of nitrogen dioxide, the presence of this gas transfers the form energy level of the nanotube to the capacitance band. This increases the concentration of pores in the nanotube, resulting in improved electrical conductivity. The researchers studied the efect of nitrogen dioxide and ammonia gas on the electrical properties of a Single walled carbon nanotube -based sensor. The response of single-walled carbon nanotube forests is less than that of single nanotube devices [[200](#page-24-3)[–203\]](#page-24-4). This result can have two reasons: In bulk single-walled carbon nanotube samples, the efects of molecular interaction are less than in metal and semiconductor nanotubes. Also, inner tubes in single-walled carbon nanotube flaments are not able to interact with gases; this

![](_page_9_Figure_1.jpeg)

<span id="page-9-0"></span>**Fig. 10** Electrical response of semiconductor nanotubes in the presence of molecules Gas with a flow of  $200$  ppm of  $NO<sub>2</sub>$  and SWNT-S in the presence of Al flow with 1 weight percentage of  $NH<sub>3</sub>$ 

is because molecules cannot penetrate the single-walled carbon nanotube strands [\[204–](#page-24-5)[206\]](#page-24-6).

Zatt et al. [[45\]](#page-19-16) found that single–walled carbon nanotube was highly sensitive to oxygen. Adding a small amount of oxygen to these nanotubes can reverse their electrical resistance, so semiconductor nanotubes can turn into metal nanotubes in the presence of oxygen. The authors of the paper stated that carbon nanotubes could be used as chemical gas sensors, but that the surrounding air could afect some of the intrinsic properties of these nanotubes. Finally, the team concluded that the charge transfer caused by oxygen to the nanotubes is a sign of structural defects in the nanotubes, and that the entry of oxygen into the nanotubes and their adsorption into the inner wall of the nanotubes should not be overlooked.

Goldoni et al. [[47\]](#page-19-30) investigated the relationship between gas sensing properties and defects and contaminants on the surface of single-walled carbon nanotubes. The team investigated the efects of oxygen, nitrogen, carbon monoxide, moisture, nitrogen dioxide, sulfur oxide and ammonia gases on the emission spectrum of nanotubes before and after vacuum heat treatment. Heat treatment on nanotubes reduces the number of structural defects in nanotubes, which are caused by purifcation or removal of contaminants such as catalyst particles. After heat treatment, the electronic spectrum of single-walled carbon nanotubes loses its sensitivity to oxygen, nitrogen, carbon monoxide and moisture, while it is sensitive to ammonia, nitrogen dioxide and sulfur oxide. Thus, some of the imagined intrinsic properties of pure nanotubes or those that are slightly heated are afected by contaminants, defects, or catalytic particles. The authors of this paper found that gas molecules in the presence of air (i.e., oxygen, nitrogen and moisture) have a weak interaction with nanotubes, i.e,. they do not form any chemical bonds with nanotubes. Therefore, in order to achieve high sensitivity in these sensors, the surface of the nanotubes must be clean and its structural defects must be controlled.

Some studies show that functionalizing the side wall of nanotubes leads to better bonding of specifc compounds with nanotubes and also improves the sensitivity and selectivity of nanotubes. For example, carbon nanotubes with a coating of palladium are sensitive to hydrogen. The concept of metal–carbon nanotube cluster hybrids as a sensitive material with a site for adsorption of diferent target molecules was introduced in a theoretical study [\[207–](#page-24-7)[210\]](#page-24-8). In this study, which was studied on CNT-AL clusters, the researchers showed that by absorbing ammonia, charge accumulation and polarization occurred in the area between the aluminum cluster and the nanotube. This load transfer provides important information about the electronic response of the system. This afects the ionic portions of the bonds and changes the position of the Fermi energy level. Therefore, changing the electrical conductivity of the CNT-Al system is used as a measure of the sensitivity of chemical sensors. Based on these theoretical results, the metal/CNT cluster hybrid can be used to identify chemical species with high sensitivity and selectivity. A key point in the strategy is to use nanoclusters that can absorb or release large amounts of charge in the presence of the target molecule. Therefore, these nanoclusters will afect the electron transfer in the nanotubes. This strategy was frst proposed by several research groups in 2006 and 2007.

Kumar et al. [\[52\]](#page-19-31) Used chemistry to create platinumcoated carbon nanotubes to produce a hydrogen-sensitive sensor.

Star et al. [[53](#page-19-22)] selectively placed elements such as Pt, Pd, Au, Rh, Sn, Mg, Fe, Co, Ni, Zn, Mo, W, V, and Cr onto carbon nanotubes to provide a sensor for carbon monoxide, nitrogen dioxide, and methane and produce hydrogen sulfde, ammonia and hydrogen. One of the challenges of this path is to be able to place metals of the same dimensions on the wall of the nanotube. If the particles are not fxed on the surface of the nanotubes, they will move and the sensor response will be unstable. Figure [11](#page-10-0) shows this problem for metal-coated carbon nanotubes. For these

![](_page_10_Picture_2.jpeg)

**Fig. 11** TEM micrograph of carbon nanotubes coated with Pd nanoparticles. The decoration is done with the selected plating method

<span id="page-10-0"></span>![](_page_10_Picture_4.jpeg)

**Fig. 12** Micrograph of multi-walled carbon nanotubes decorated with gold nanoparticles. Gold particles it is mobile and is applied on the obtained nanotubes and gold nanoparticles they are evenly distributed and located on the defective points. This nanotube using Plasma is activated

<span id="page-10-1"></span>nanotubes, plating method with selected position has been used. This problem can be solved by adopting a method of operating cold active plasma, such as oxygen plasma on nanotubes. This approach allows nanomaterial engineers and designers to produce hybrid nanostructures in a single step, without the need for steps such as activation, functionalization, or cleaning. The plasma method allows to control the shape, dimensions, coordination and penetration of metal nanoparticles on nanotubes. Figure [12](#page-10-1) shows the plasma operation that causes the nanoparticles to settle uniformly on the wall of the nanotubes. Metal atoms are not stationary and are constantly moving, these atoms continue to move until they reach the nucleus. The oxygen plasma method can create diferent nuclei on the nanotube. This was previously predicted using computational studies. In addition, oxidation operations afect the density states of the capacitance bands and increase the working function of pure nanotubes. The working function of nanotubes treated with oxygen plasma is very close to metals such as platinum, gold, palladium and nickel. This facilitates the movement of electrons between nanoparticles and nanotubes. The direction of charge movement depends on the surrounding gaseous environment. The interaction between nanoparticles and nanotubes

![](_page_10_Figure_7.jpeg)

<span id="page-10-2"></span>**Fig. 13** Optical microscope image of a 4-element sensor array. The image SEM of the electrode representing the bridge created by the CNT. TEM image of Pd coated nanotubes and image of Rh-coated nanotubes

![](_page_10_Figure_9.jpeg)

<span id="page-10-3"></span>**Fig. 14** Curve of response and reduction in CNT-Rh sensors. These sensors at room temperature and in Operated at a temperature of 150 °C

facilitates the identifcation of gases by nanotubes, which is done by changing the electrical conductivity of hybrid nanomaterial.

Haick et al. [[73\]](#page-20-24) identified benzene using plasmaprocessed arrays. In this study, researchers used metalwalled multi-walled carbon nanotubes. The limit of benzene measurement was less than 50 ppb and the detection process was performed by changing the humidity in the presence of disturbing species such as carbon monoxide, hydrogen sulfde and nitrogen dioxide. Figure [13](#page-10-2) shows a

four-element sensor. Figure [14](#page-10-3) shows the response of an Rh-walled multi-walled nanotube sensor to benzene.

Penza et al. [[62–](#page-20-25)[64\]](#page-20-26) used the sputtering method to decorate the nanotubes with Au, Pt, Pd, Ru, and Ag particles. Plasma method helps to functionalize the products obtained from sputtering. This method has been used successfully to functionalize nanotubes grown in CVD, without the need to transfer the nanotubes to another device for functionalization. Researchers have developed sensors to detect nitrogen dioxide, ammonia, hydrogen, hydrogen sulfde and carbon monoxide. Although few studies have been performed on metal cladding of nanotubes, this method is frequently used to improve the selectivity of nanotubes. When the ratio between plasma nanotubes and metal oxide is appropriate, hybrid sensors can perform well at room temperature, allowing the detection of carbon monoxide and nitrogen dioxide in the ppm concentrations. These optimized sensors are less sensitive to the negative efects of moisture. There have been few successes in enhancing nanotube replacement to increase the sensitivity and selectivity of nanotubes. The addition of boron and nitrogen can improve the electrical conductivity of nanotubes. Nitrogen-reinforced carbon nanotubes are highly efficient in identifying hazardous gas molecules due to the presence of pyridine sites on the surface of the nanotubes. The researchers found that nitrogen-reinforced nanotubes had a very short reduction time for ammonia detection. These nanotubes also respond very strongly and reversibly to ethanol. Various studies have shown that no charge exchange occurs between carbon monoxide and nanotubes. However, calculations show that it is possible to use reinforced carbon nanotubes to detect carbon monoxide. Various researchers have investigated the modifcation of nanotube walls with organic molecules to improve their sensitivity.

Johnson et al. [[83\]](#page-20-15) Showed that sensors based on religious strings can perform well. In these sensors, the world is used as an identifcation site. The researchers showed that these sensors were able to react to the smell of explosive gases and nerve toxins, something that is not seen in pure nanotubes. These sensors can be used to detect and quantify gases if they have a specially sequenced diode.

Penza et al. [[62–](#page-20-25)[64](#page-20-26)] investigated the sensory properties of Porphyrin/carbon nanotube flms. They investigated the possibility of changing the absorption efect of the Porphyrin layer to change the strength of the nanotube layer. The presence of porphyria flms increases the selectivity of the electrical resistance of nanotubes to volatile compounds. This is due to the high efficiency of metal-coated Porphyrin in transferring charge from adsorbent molecules to nanotubes. The researchers suggested that the selectivity of these sensors could be improved by using diferent metal compounds in the body of the Porphyrin. One of the main problems

![](_page_11_Figure_7.jpeg)

<span id="page-11-0"></span>**Fig. 15** Sensory response to diferent concentrations of **a** hexanol in dry air. **b** Acetone in dry air and humidity 80%. Red curve: response generated by a single-walled carbon nanotube sensor. Black curve: the response generated by the carbon nanotube sensor PAH functionalized single wall

in the commercialization of these nanotube sensors is the changes in humidity in the environment.

Novoselov et al. [\[80](#page-20-23), [81](#page-20-20)] came up with an interesting idea to solve this problem. They poured a drop of purifed singlewalled nanotube onto a silicon surface and made nanotube electrodes. These electrodes were coated with polycyclic aromatic hydrocarbon compounds (PAHs). PAHs have alkyl groups that can self-assemble into large, electron-rich molecular groups that can guarantee good charge transfer. Nanometer-thick PAH columns easily form a three-dimensional, spongy structure with a high volume-to-surface ratio. Multi crystalline PAH layers are formed on the surface of nanotubes by casting. Using the right combination of PAH and SWNT, an accurate sensor with high selectivity can be

developed that can distinguish polar organic volatile compounds from non-polar ones, so that the ambient humidity can vary from 5 to 80% (Fig. [15](#page-11-0)). These fndings show that the research process is moving towards the construction of inexpensive, lightweight, low-consumption and non-destructive sensors that are able to identify a wide range of volatile organic materials in our environment.

Liu et al. [[87\]](#page-20-17) Used single-walled carbon nanotubes with amino phenyl and amino Cyclodextrin functional groups to identify organic contaminants. These sensors are able to detect organic contaminants, and in the presence of these contaminants, there are drastic changes in their electrical conductivity. Star Group recently developed a single-walled carbon nanotube-based sensor using copper complex that can selectively detect 0.5 ppm ethylene.

When single-walled carbon nanotubes are used as feldefect transistors in nano sensors, they have high selectivity and low energy consumption. These nanotubes can be used in various devices, but due to the presence of impurities, a purifcation process must be applied on them. When feldefect transistors operate in ambient conditions (ie, variable ambient humidity), the device undergoes a great deal of stress [\[211](#page-24-9)[–214\]](#page-24-10).

Kaner et al. [\[86](#page-20-16)] proposed a method in which individual nanotubes grow directly between the non-metallized parts of the device. Pd is then layered on this structure using shadow masks. This new system can work without stress in diferent humidity. This fnding opens a new path for highly sensitive nano sensors containing intact carbon nanotubes.

# **4 Methods of making grapheme**

## **4.1 Mechanical delamination method**

This method, which is the frst method of making graphene, involves separating graphene sheets from natural graphite with HOPG (Fig. [16\)](#page-12-0). Separating graphene sheets from each other using glue is possible and is a simple, inexpensive, yet low-efficiency, randomly generated plate production method [\[215,](#page-24-11) [216,](#page-24-12) [257–](#page-25-4)[260](#page-25-5)]. In this method, after gluing graphite pieces together several times and reducing the number of layers, fnally the adhesive tape containing graphene plates can be transferred on a 300 nm substrate of silicon and using light microscope, AFM or Raman spectroscopy microscope, the number and distribution of layers (Figs. [17,](#page-12-1) [18](#page-13-0), [19](#page-13-1)). Identifed graphene. The better the structural structure of the original graphite and the larger the dimensions, the larger and less fawed the detached graphite plates will be. The highest quality graphene for research studies with a mobility of about 40,000 cm<sup>2</sup> v<sup>-1</sup> s<sup>-1</sup> for carriers, but due to the random results and uncontrollable efficiency in obtaining graphene components is practically not capable

![](_page_12_Figure_9.jpeg)

<span id="page-12-0"></span>**Fig. 16 a** Image of direct delamination of graphene onto polyimide substrate. Throughout the operation, no sacrifcial Poly (methyl methacrylate) help is used. **b** Direct delamination time-lapse optical images; the whole process takes 5 min [[95](#page-21-22)[–97\]](#page-21-3).

![](_page_12_Figure_11.jpeg)

<span id="page-12-1"></span>**Fig. 17** SEM photographs of CVD-grown graphene **a** prior to direct delamination (on Cu) and **b** after direct delamination (on polyimide) [[95](#page-21-22)–[97](#page-21-3)]

<span id="page-13-0"></span>**Fig. 18** AFM photographs of  $0 \mu m$ graphene **a** grown on Cu, **b**  $(a)$ directly delaminated with polyimide support/substrate, and **c** delaminated onto a prepared polyimide substrate with poly (methyl methacrylate) [[95](#page-21-22)–[97](#page-21-3)]  $1x10<sup>4</sup>$  $(a)$ Photoelectron intensity (cts/s)  $8x10$  $6x10$  $\circ$  $4x10$  $\Pi \rightarrow \Pi'$ transition  $2x10$ 0 285 290 280 Binding energy (eV)  $7x10<sup>4</sup>$  $\mathsf{h}(\mathsf{b})$ Photoelectron intensity (cts/s)  $6x10$  $\frac{G}{4}$  $5x10$  $\mathcal{O}$  $4x10$  $3x10$  $\frac{5}{2}$  $2x10$  $1x10$ 

200 400 600 800 1000 1200  $\Omega$ Binding energy (eV)

<span id="page-13-1"></span>**Fig. 19 a** Specifcally delaminated graphene XPS C 1 s spectrum on a polyimide backing there's also a Gaussian/Lorentzian ft. The various peaks in polyimide and graphene lead to diferent carbon atom bonding confgurations. **b** There are no inorganic chemicals in the XPS survey spectrum (at the threshold detection limit) [\[95–](#page-21-22)[97\]](#page-21-3)

of large-scale industrialization. Figure [20](#page-13-2) shows a variety of manufacturing methods and a comparison between quality and mass production capabilities of each [\[95–](#page-21-22)[97,](#page-21-3) [261](#page-25-6), [262](#page-25-7)].

## **4.2 CVD chemical vapor deposition method**

In this method, a hydrocarbon is decomposed as a carbon source and a layer or layers of graphene are grown on the metal substrate. Since this method has an acceptable speed

 $\circ$ 

![](_page_13_Figure_8.jpeg)

 $0 \mu m$ 

 $(c)$ 

 $252$ 

<span id="page-13-2"></span>**Fig. 20** Demonstration of diferent manufacturing methods and comparison between quality and mass production capability of each [[95–](#page-21-22) [97\]](#page-21-3)

of production, good quality, and the possibility of mass production, it has been considered since 2010. The metal layer, which is usually composed of nickel, copper [[98\]](#page-21-23) and other intermediate metals such as Pd [[98](#page-21-23)], Pt [[100\]](#page-21-4), Rh [[101](#page-21-5)], and Ir [\[102\]](#page-21-24), acts as a catalyst in the formation of carbon covalent bonds. The presence of grains and defects in the metal substrate is transferred to graphene, and the resulting graphene is a kind of polycrystalline, and the mobility of the carriers is of the order 15,000 cm<sup>2</sup> v<sup>-1</sup> s<sup>-1</sup>.

## **4.3 Chemical method**

 $0 \mu m$ 

 $(b)$ 

23.2  $\epsilon$ 

 $15.0$ 

 $10.0$ 

 $50$ 

This method involves oxidizing the graphite layers and so permeating the oxidized layers as graphene oxide. Hammers in 1958 [[104\]](#page-21-25) was ready to provide an optimal method for oxidation of graphite using acid and permanganate. By weakening the van der Waals bonds between the plates in grapheme within the oxidation process, the space between the plate's increases to 0.75–0.65 nm. In grapheme oxide, the oxidation groups of  $sp<sup>2</sup>$  hybridization convert graphene to  $sp<sup>3</sup>$  and introduce a special inventory, especially

 $15.0<sub>nn</sub>$ 

electrically. Graphene oxide reduction means the removal of oxide groups and therefore the recovery of sp2 hybridization, referred to as Reduced Graphene Oxide (RGO), which is 4 or 5 times less electrically resistant than grapheme oxide. This method, while cheap and mass-produced, may be a colloidal candidate for industrial applications, especially within the felds of polymer composites and hybrid nanostructures. However, the tiny size (between 1 and 5 microns) of the plates and therefore the presence of oxide residual groups and structural defects because of oxidation processes and reduction of electrical mobility of order  $1 \text{cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ , which is not recommended for electronic and transistor applications. Figure [20](#page-13-2) provides a comparison between graphene manufacturing methods in terms of quality and production capacity, which may be a summary of this section [[217–](#page-24-13)[219\]](#page-24-14).

#### **4.4 Graphene‑based sensors**

In 2007, Shedin et al. [[105](#page-21-6)] were able, as the frst grapheme sensor report, to absorption and desorption the gas molecule from HOPG laminated graphene without any physical or chemical activation and only by removing the contaminants deposited on the graphene during electrode fabrication. This group was able to measure the presence of electron accepting gases such as  $I2$ ,  $NO<sub>2</sub>$ , and  $NH<sub>3</sub>$  and electron donor gases such as NO,  $H<sub>2</sub>O$ , and CO in the controlled conditions (2) ppb) (Fig. [21\)](#page-14-0). From the Hall Effect test, Shedin et al. [[105\]](#page-21-6) Proved that the presence of electron acceptor (donor) gases leads to the injection of a cavity (electron) of the order of  $1012 \text{ cm}^2$  into grapheme. Gas absorption causes the dispersion of carriers from these additional injected loads, which according to the report of this group, in comparison with the reduction of carrier mobility due to impurities, the efect of change in the density of charge carriers is dominant [[220](#page-24-15)[–222\]](#page-24-16). The group also attributed the oscillations and steps in the dynamic response of an electric current to the absorption and desorption of gas molecules. One of the

challenges of grapheme sensing is the absorption of gaseous molecules that require energy and do not occur spontaneously due to the active carbon level of grapheme. For graphene obtained from sensor mechanical sheet up to 25ppt in the presence of  $NH<sub>3</sub>$ , NO and NO<sub>2</sub> gases have been reported [[106,](#page-21-7) [250–](#page-25-8)[252\]](#page-25-9). The interesting thing about this work is the use of UV rays during the desorption process. UV radiation in the presence of oxygen leads to the production of reactive oxygen species, which clean the graphene surface and facilitate the adsorption process. It is unlikely to have a clean and unpolluted graphene after the manufacturing process. The presence of these residual contaminants on the graphene surface can act as a sensitizer and improve its sensitivity to the clean sample. In a report, Johnson Group [[107,](#page-21-9) [253–](#page-25-10)[256](#page-25-11)] showed that the presence of polymers left over from the manufacturing process can act as an adsorbent and improve the sensor one or two times, because after removing these polymer contaminants by heating the process in  $Ar/H<sub>2</sub>$ at 400 °C. The mobility of the carriers increases fourfold and the density of the contaminated loads decreases by one-third and their sensitization decreases by one or two times. Other polymers such as PMMA (Poly methyl methacrylate) and PANI (Polyaniline) have a similar effect on graphene. The use of three-dimensional graphene structures grown by CVD on porous nickel and copper foams is a novel way to make graphene sensors [\[108](#page-21-10), [109](#page-21-26)]. These foams act as a mold and catalyst for the growth of graphene and are removed with a chemical solution after growth. This three-dimensional graphene network has a large surface area (Fig. [22\)](#page-15-0) and is electrically and mechanically interconnected. Because the graphene mesh may collapse after removing the metal foam, the PMMA polymer layer is used as a backing.

Robinson et al. [\[110,](#page-21-11) [111,](#page-21-12) [243](#page-25-12)–[246](#page-25-13)] in their frst study on RGO sensors in 2008 showed that both regions with  $sp<sup>2</sup>$ and  $sp<sup>3</sup>$  orbitals (graphene domains and graft defects) play an important role in the sensor [\[247](#page-25-14)[–249\]](#page-25-15). In this report, GO plates were placed on metal electrodes as a network of interconnected plates and the sensor response of the

<span id="page-14-0"></span>![](_page_14_Figure_7.jpeg)

![](_page_14_Figure_8.jpeg)

![](_page_15_Figure_2.jpeg)

<span id="page-15-0"></span>**Fig. 22 a**, **b** The three-dimensional structure of graphene and its sensory response behavior to **c** NO2 and **d** NH3. During desorption, 400 K heating is applied [[108\]](#page-21-10)

<span id="page-15-1"></span>![](_page_15_Figure_4.jpeg)

![](_page_15_Figure_5.jpeg)

samples with diferent reduction times was investigated (Fig. [23\)](#page-15-1). According to the fndings of this group, the rate of graphene reduction afects the noise and gas sensitivity, because with increasing the rate of reduction of graphene and areas with  $sp<sup>2</sup>$  hybridization, less response and adsorption times were observed [[263](#page-25-16)]. Therefore, it can be said that areas with  $sp<sup>2</sup>$  orbital are low energy locations for rapid gas adsorption and adsorption, while slower absorption and desorption occur with stronger binding in  $sp<sup>3</sup>$  and defective areas. The group showed that by increasing the thickness of the RGO layer, the amount of electrical noise is also reduced compared to nanotubes, and to study the selectivity of four toxic gases such as CEES, DMMP, HCN and DNT were tested.

# **5 Gas sensors based on graphene oxide‑metal two‑component structures**

Catalytic metals like platinum (Pt) and palladium (Pd), when placed on RGO plates, form a weak Schottky barrier when properly interacted with. This Schottky barrier depends on the function of the metal and the way it interacts with the graphene plate. This Schottky barrier dam is incredibly sensitive to gas absorption and injection of carriers and results in many relative changes in current and voltage for instance, during a report on the Pd-RGO hybrid structure, [[112](#page-21-8), [223,](#page-24-17) [224\]](#page-24-18) a Schottky barrier dam is formed of type n, and with the presence of gas and interaction with Pd, the metal working function changes, leading

<span id="page-16-0"></span>**Fig. 24 a** Stages of construction of Pd-RGO hybrid structures and design of Schottky dam formed in the interphase and **b** Sensor results for NO gas [[112\]](#page-21-8)

![](_page_16_Figure_2.jpeg)

to a decrease in Schottky barrier dam height and a rise in flow. (Fig. [24](#page-16-0)). On the opposite hand, NO, as a gasified, can exchange charge with the hybrid system and increase conduction. Table [1](#page-16-1) shows the reports on graphene-metal oxide hybrid sensors.

# **6 Gas sensors based on graphene oxide‑metal oxide two‑component structures**

6000

Time (s)

Many of the existing and well-known sensors are metal oxide based sensors, also known as solid state sensors.

Graphene-RGO (B)

9000

<span id="page-16-1"></span>![](_page_16_Picture_224.jpeg)

![](_page_16_Picture_225.jpeg)

 $0.00$ 

 $\overline{\circ}$ 

3000

The basis of these sensors is the absorption of oxygen groups as  $O^{2-}$ ,  $\overline{O}$  and  $O^{-2}$  on the surface and the change of the Schottky barrier between the metal oxide boundaries. By absorbing these oxygen groups as lethal electron groups (with high electronegativity), the metal oxide of one electron participates and traps electrons from the sur-face to the trap levels of the resulting electron trap [[115,](#page-21-15) [225,](#page-24-19) [226\]](#page-24-20). This migration of electrons from the surface to the mass creates an empty layer of electrons on the surface, especially in the grain boundaries, and the width of this layer increases with the absorption of more oxygen groups. However, the presence of grapheme as a good conductor with a suitable working function can play an important role in sensing hybrid structures with metal oxides  $[227-229]$  $[227-229]$  $[227-229]$  $[227-229]$  $[227-229]$ . In general, the effects of the presence of RGO plates on a metal oxide hybrid structure can be divided into three categories: increased electrical conductivity of the hybrid layer due to the good conductivity of graphene plates; Semiconductors with a gap band greater than 1 eV usually have high electrical resistance at room temperature, and the presence of graphene plates as fast fow channels can provide adequate conductivity for the sensor at lower temperatures [[116](#page-21-16), [117](#page-21-17)]. Graphene itself can act as a sensory component and increase the sensitivity of the hybrid layer when the whole surface of graphene isn't coated with metal oxide nanostructures. When the area of graphene is high, grapheme forms a typical bond with metal oxide as a substrate [[230](#page-24-23)–[234\]](#page-25-17). The charge exchange between grapheme and metal oxide is restricted to those areas and also the potential barrier in these areas is additionally very sensitive to gas absorption [\[118,](#page-21-27) [119](#page-21-28)]. Therefore, the amount and type of active sensor sites and sensor sensitivity increases with the presence of graphene. Figure [25](#page-17-0) shows a diagram of the mentioned maps. In fact, graphene in a very hybrid layer practically creates more and more sensitive areas for gas access by improving the conduction, increasing and modifying common seasons, the width of the empty layers, and also the height of potential dams. On the opposite hand, graphene as a substrate can cause new nucleation on itself, thus reducing the further accumulation of metal oxide nanostructures and thus increasing the effective expanse of the layer. This effect, unlike CNTs, is restricted to the two-dimensional structure of graphene.

<span id="page-17-0"></span>**Fig. 25 a** Scheme of the efect of the presence of grapheme in a hybrid layer with metal oxide, **b** Design in the absence of graphene in a hybrid layer with metal oxide [[120](#page-21-29), [121](#page-21-18)]

![](_page_17_Figure_5.jpeg)

# **7 Conclusion and perspective**

Over the years, many researchers have turned their attention to carbon nanomaterials. The unique optical, mechanical and electronic properties of these nanostructures have led them to use these nanomaterials to develop small devices, such as energy-saving sensors. In this review, we will cover the work on carbon nanotubes used in sensors. In particular, examples of carbon nanotubes that play a key role in devices that are sensors of biomolecules, gas, light and pressure changes. Carbon and graphene nanotubes are among the most important nanostructures used in industry. This is due to their extraordinary mechanical, electrical, thermal and optical properties. These nanostructures are widely used in the manufacture of items such as nanocomposites with special properties and electronic devices. For both of these nanostructures, there are many challenges in the controlled synthesis and economization of industrial production, and signifcant advances have been made over time. In case of producing controlled, quality and cheaper samples, these two nanostructures have a lot of potential for the evolution of many industries. Today, the unique electronic properties and structures of carbon nanostructures, such as nanotubes, regenerated graphene, and graphene oxide, are used to make sensors. However, the industrial and commercial production of these sensors is not yet successful and there is a need for improvements in this technology. The frst challenge in this direction is to fnd a cheap way to mass produce these sensors. If pure carbon nanotubes or pure graphene are needed to make the sensor, the CVD growth method is the best choice. Although some studies have shown the production of very pure single carbon nanotubes with this method, due to the humidity of the environment, stresses occur on the nanotubes. Much research needs to be done on the growth of carbon nanotubes to establish predetermined metal or semiconductor properties in these nanostructures.

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## **Declarations**

**Conflict of interest** The author declare that they have no competing interests.

**Research involving human participants and/or animals** This work does not contain any studies with human participants or animals performed by any of the authors.

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