We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Graphene and Its Nanocomposites Based Humidity Sensors: Recent Trends and Challenges

*Avik Sett, Kunal Biswas, Santanab Majumder,
Arkaprava Datta and Tarun Kanti Bhattacharyya*

Abstract

Humidity sensors are of utmost importance in certain areas of life, in processing industries, in fabrication laboratories and in agriculture. Precise evaluation of humidity percentage in air is the need of various applications. Graphene and its composites have shown great potential in performing as humidity sensors owing to enormous surface area, very low electrical noise, high electrical conductivity, mechanical and thermal stability and high room temperature mobility. There is no such extensive review on graphene-based devices for humidity sensing applications. This review extensively discusses graphene-based devices intended towards sensing humidity, starting from the methods of synthesizing graphene, its electronic and mechanical properties favoring sensing behavior and different types of sensing mechanisms. The review also studies the performance and recent trends in humidity sensor based on graphene, graphene quantum dots, graphene oxide, reduced graphene oxide and various composite materials based on graphene such as graphene/polymer, graphene/metal oxide or graphene/metal. Discussions on the limitations and challenges of the graphene-based humidity sensors along with its future trends are made.

Keywords: Humidity sensors, Synthesis of graphene, Graphene oxide, Graphene quantum dots, Graphene/2D materials

1. Introduction

Humidity sensors is one of the habitual sensors used in our regular activities. It plays a significant part in controlling humidity in certain application areas such as monitoring moisture in agriculture, processing industry, device fabrication laboratories, monitoring indoor air quality, controlling domestic instruments, medical applications and in weather forecasting [1, 2]. Humidity sensors detects the amount of water in the atmosphere and transforms it into a measurable signal. After interaction with the water molecules, the physical parameters of the humidity sensors are observed to change. These parameters decide on the category of humidity sensor such as resistive, capacitive, optical-fiber, impedance, surface-acoustic wave (SAW), Quartz crystal microbalance (QCM) and resonance type [3]. Many ultra-sensitive materials have been developed towards detection of water molecules such as ceramics (Al_2O_3 , SiO_2 etc.) [2], perovskite compounds [4, 5], semiconductors

(SnO₂, ZnO, etc.) [6, 7], semiconducting and conducting polymers [8] and 2-D materials such as MoS₂ [9], WS₂ [10], black phosphorus [11], carbon nanotubes [12] and graphene [13].

Graphene and graphene based composite nanomaterials in this context is attracting significant attention due to its fascinating and unique electrical, mechanical and optical properties. Various methods of graphene synthesis have been discovered such as sublimation of silicon carbide (SiC) at high temperature, chemical vapor deposition (CVD), mechanical exfoliation etc. However, to ensure the availability of graphene-based sensor devices widely to the society, cost of these sensors must be as low as possible and large-scale production of graphene should be feasible. Production of chemically derived graphene by reducing graphene oxide is an economical process and requires very user friendly and low-cost equipment and resources. Modified Hummers method-based synthesis of graphene is well known. Various reducing techniques of graphene oxide leads to the formation of chemically derived graphene (reduced graphene oxide) with different functional groups attached to it. Chemically derived graphene induces several defects on its matrix compared to pristine graphene. These defect sites act as electroactive and optical centers for sensing applications. Tuning the mechanical, optical and electrical properties of graphene for various sensing applications can be done quite efficiently by i) metal doping, ii) decorating it with nanoparticles, iii) selectively reducing the functional groups, iv) making nanocomposites with metal oxide nanoparticles or polymers and many more.

Even though there are some articles related to progress of chemical, tactile and gas sensors based on graphene [14, 15], there are no such review article on humidity sensors based on graphene. The main focus of this review is to discuss the recent advances in humidity sensors based on graphene. The review is partitioned into three parts: Synthesis of graphene and its related properties favoring sensing phenomenon, sensing mechanism of different humidity sensors and advances made in graphene and its composite towards fabrication of humidity sensors. The synthesis part explains the different methods of preparing pristine graphene, chemically derived graphene and also describes the different properties of graphene that facilitates the use of graphene as a sensing material. The different mechanisms include seven types of graphene-based humidity sensors and its description. The last part discusses the progress made in humidity sensor development using graphene and graphene-based composites as sensing material. Finally, challenges faced by graphene-based humidity sensors and the outlook towards future research and developments are discussed.

2. Graphene as a transducing material owing to its properties

Graphene is a sp² hybridized honeycomb like structure with an array of carbon atoms featuring a bond length of 1.42 Å and 120° angles. It is a monolayer structure being established as the thinnest form of carbon nanomaterials and probably the thinnest material discovered. The symmetry of this two-dimensional lattice gives rise to some fascinating electronic and mechanical properties. Graphene is known to be the strongest material ever found [16] with an ability to be bent without affecting its internal structure and properties. Graphite being the parent material, comprises stacking of several graphene layers on top of one another having an inter-layer separation of 3.354 Å [17]. There are two different ways in which the graphene layers could be stacked as shown in **Figure 1**. Eighty percent of the graphite found in nature is the Bernal graphite, an allotrope of graphite comprising ABA stacking configuration. Fourteen percent of the graphite found is of the type rhombohedral

Figure 1.
 Bernal (ABA) and rhombohedral (ABC): The two stable allotropes of graphite.

with ABC stacking configuration, whereas the rest six percent is disordered in nature having no such stacking configuration. Single layer graphene is very difficult to obtain and it has very low yield. Hence few layered graphene is considered in most of the cases for device fabrication towards heavy metal sensors, as its properties are in between that of graphite and single layer graphene, with high mechanical and electrical stability. However, both single layer and few layered graphene can be used towards sensing application after proper functionalization.

2.1 Electronic properties

The formation of perfect honeycomb lattice from the arrangement of carbon atoms results in electronic properties of graphene. Hybridized orbitals that are sp^2 in nature is the backbone of graphene. The p orbitals that are perpendicular to the lattice is responsible for conductivity in the graphene matrix. These orbitals get conjugated to form conduction bands (π^*) and valence bands (π), which are significant towards sensing of various analytes. The transduction of the interaction between the graphene-based materials and the analytes to a readable electrical signal is facilitated by these orbitals. The fermi level of pristine graphene is located exactly in the position where the conduction and valence bands meet. Altogether, in the Brillouin zone, there are six such points where conduction band meets valence band. These points are termed as neutrality points or Dirac points and in the reciprocal space, it is labeled as K and K' [18]. The ability of electrons in graphene to travel sub-micron distances without any scattering (travel without electrical resistance) is known as ballistic transport. This type of transport in graphene is observed at room temperature and is not affected by the adsorbates present in the graphene matrix or the substrate's topography [19]. Even though at room temperature, impurity scattering limits the mobility of charge carriers, the mobility of carriers in graphene stays very high even at the presence of chemical and electrical dopants at high concentrations [20]. Electrical robustness of graphene-based sensors is attributed to these types of transport phenomenon. Tuning of charge carriers between holes and electrons for doping graphene is possible due to the presence of strong ambipolar electric field effect. This facile modulation of graphene field effect transistors allows detection of n-type and p-type analytes with very high sensitivity, as will be discussed later. At the fermi level, the conductivity of graphene does not get vanished as conductivity of graphene is quantized. Eventually, at the fermi level where density of states approaches zero, there still exists finite conductivity. The last charge carrier provides e^2/h as the minimum conductivity [18]. Hence, graphene is found to have no transition of metal-insulator while measurement of $\sigma_{\min}$. The experimentally obtained value for $\sigma_{\min}$ is found to be $4e^2/h$. The electronic property of graphene changes with change in the number of

graphene layers. At one horizon, single layer graphene is a semiconductor having zero band gap (semimetal having zero overlap) and on the other horizon, graphite is found to be a semimetal having a band overlap of 41 meV. With respect to the properties of graphene, the threshold between bulk and single layer graphene is not much clear. With increase in the number of graphene layers, the band overlap starts increasing till it reaches that of the bulk graphite. The amount of overlap seems to be a decent indicator of the threshold between 2D and 3D behavior of graphene. It is observed that, for graphene with more than 11 layers, the overlap is seen to vary only 10% compared to that of bulk graphite. Hence, 10 layers are suggested to be the limit to few layers' graphene. Therefore, single layer graphene as well as few layers graphene (up to 10 layers) can be used towards water contaminant and heavy metal detection.

2.2 Mechanical properties

Molecular dynamics-based simulations are carried out to investigate the fracture strength and Young's modulus of single layer graphene. Measurements related to force-displacements by AFM (atomic force microscopy) was conducted to analyze the Young's modulus of few layer graphene. The AFM measurements were conducted on strips of graphene after being suspended over trenches. Measurements using AFM by nanoindentation was conducted to measure the intrinsic breaking strength and other elastic properties of graphene [21]. Defect free single layer graphene was found to have fracture strength of 130 GPa and Young's modulus of 1.0 TPa.

3. Synthesis of graphene for humidity sensors

Synthesis of graphene can be categorized into two different approaches, top-down and bottom-up. Top-down approaches deal with exfoliation of bulk graphite into single layer (or few layer) graphene. Bottom-up approaches include pyrolysis, epitaxial growth, chemical vapor deposition and plasma synthesis.

3.1 Top-down techniques

The top-down technique deals with attacking the raw bulk graphite and separate the layers to obtain sheets of graphene. Mechanical and chemical exfoliation of bulk graphite powder results in single to few layers of graphene sheet characterized by Raman spectroscopy.

3.1.1 Mechanical exfoliation

Exfoliation of bulk graphite mechanically to extract single layer to few layer graphene sheets over desired substrates is a well-known method. The superficial part of the graphite experiences longitudinal or transverse stress during mechanical exfoliation. The interlayer distance between graphene layers is 3.354 Å and the value of bond energy is found to be 2 eV/nm². The external force required for mechanical cleaving of graphite layers to obtain single atomic layer graphene sheet is approximately 300 nN/mm². When the partially filled p-orbitals overlap perpendicularly on a plane sheet, the van der Waals forces results in stacking of the sheets. The higher lattice spacing in vertical direction and poor bonding forces between the layers causes the reverse step of stacking, exfoliation to occur when external forces are applied. This mechanical exfoliation is carried out by peeling layers from different

graphitic substances such as HOPG (highly ordered pyrolytic graphite), natural graphite and monocrystal graphite. Mechanical exfoliation is generally carried out using different agents such as ultrasonication, electric field and scotch tape.

3.1.2 Chemical reduction of graphite oxide

One of the top-down approaches to produce enormous amount of graphene is through chemical reduction of graphite oxide. Synthesizing graphite oxide requires oxidation of graphite, which is usually done by utilizing certain oxidants such as potassium permanganate, concentrated nitric acid and sulfuric acid. In 1860, graphene oxide was first produced by Brodie, Staudenmaier and Hummers. After this discovery, modified Hummers method and Improved Hummers method were created [22]. Major differences between these methods are the types of oxidants, the number of steps and degree of toxicity. With progress, the toxic nature of synthesis could be eliminated with decrease in reduction steps. Once the oxidation is complete, various reducing agents are employed to remove the oxidizing groups from graphene oxide. The reducing agents may be sodium borohydrate, hydroxylamine, glucose, pyrrole, ascorbic acid, phenyl hydrazine and many more. Formation of reduced graphene oxide suspensions in organic solvents is of common practice, because graphene oxide is hydrophilic in nature, but reduced graphene oxide is hydrophobic, which leads to agglomeration of graphene sheets. Chemical reduction of graphene oxide is a very famous technique among the research community due to i) large quantity of graphene sheets, ii) desired functionalization of graphene sheets for various applications including sensing; transparent conducting electrodes for solar cell; electrochemical high energy electrode material for energy storage and many more; and iii) tuning defects or presence of functional groups by various approaches of reduction.

3.2 Bottom-up techniques

Bottom-up techniques deal with formation of graphene from carbonaceous species in vapor state. The formation of graphene from atoms of carbon results in defect free pure graphene sheets. However, the yield of graphene which is low in such cases, should be improved. Bottom-up strategies include pyrolysis, epitaxial growth, CVD, plasma synthesis and many more.

3.2.1 Pyrolysis

The pyrolysis technique comprises of formation of graphene sheets chemically by solvo-thermal method. For example, one may use 1:1 molar ratio of sodium and ethanol in a container vessel during the entire duration of thermal treatment. Another approach is pyrolyzation of sodium ethoxide through the process of sonication. This results in better performance towards detachment of graphene sheets.

3.2.2 Epitaxial growth

One of the methods to grow graphene on substrate surfaces is epitaxial growth. Graphene can be prepared by heating and cooling down a crystal of silicon carbide (SiC) at an optimum pressure. Graphene can grow on both silicon and carbide face. Growth over silicon face of the crystal leads to the formation of monolayer or bi-layer graphene. However, growth on the carbide face of the crystal leads to the formation of few layer graphene [23]. The parameters used during the growth process i.e. temperature, heating rate (ramp) and pressure facilitates the quality and

nature of graphene produced. In case, high temperature and pressure is applied, growth of carbon nanotubes is favored compared to graphene. Hence, by varying the conditions, different morphology and materials can be obtained such as carbon nanotube, graphene sheets, graphene nanoribbons etc. The lattice of Ni(III) surface is very close to that of graphene with a difference of only 1.3%. Hence, by approach of nickel diffusion [24], a thin layer of nickel might be evaporated onto the SiC crystal surface. After heat is applied, graphene will be found on the surface due to diffusion of carbon through the nickel layer. However, the entire process depends on the temperature and heating rate. This additional layer of nickel allows better separation of graphene grown on the surface of silicon carbide crystal. However, due to the formation of defects and grain boundaries, the quality of graphene is not the best and the as formed graphene lacks homogeneity.

3.2.3 Chemical vapor deposition (CVD)

CVD is one of the best techniques to produce high quality graphene sheets. It is basically a technique which involves reaction in the gaseous phase and deposition onto a desired substrate [25]. The combination of gaseous species in a reaction chamber occurs at a desired optimum pressure and temperature. When the reactant gases meet the substrate in a heated reaction chamber, a material film is seen to grow over the substrate. There are certain by products in the chamber, which are removed during the process. The temperature of the substrate plays a significant role to facilitate proper reaction mechanisms. The speed of deposition of material over the substrate is very low and in the range of few microns per hour. Two types of CVD are widely used, namely, ultra-high vacuum chemical vapor deposition (UHVCVD) and low-pressure chemical vapor deposition (LPCVD).

4. Graphene based humidity sensing mechanism

In this section, various varieties of graphene-based humidity sensing mechanism have been explored, which identifies the intrinsic mechanism involved with the water molecules in connection with the graphene's surface architecture. The interface between the available water molecules over the surface of graphene material makes a net deflection in the signal response making it an ultrasensitive sensing material for humidity sensing approach. This section highlights five types of sensing mechanisms for graphene-based humidity sensors, which includes the SAW, FET, resistive, capacitive and optical fiber-based sensing mechanisms.

4.1 Humidity sensors based on field-effect transistor (FET)

Owing to the ease of miniaturization, nature of portability, higher sensitivity, FET based Gas sensing has been designed for widespread applications [26]. Typically, a graphene-based humidity sensor comprises of graphene as the channel material, a thin dielectric layered gate electrode (**Figure 2**) and source and drain electrodes, respectively. It is through the dielectric layer; a bias voltage is usually applied on the gate electrode which has the role to modulate the graphene channel's intrinsic conductivity. It is under a constant applied gate voltage; the net humidity sensing is usually measured by measuring the current change of the graphene channel before and after exposing the channel to humidity environment. Usually, the underlying mechanisms associated with the change in the current response lies in the fact that whenever the water or gaseous molecules comes into the closer

Figure 2.
 Schematic of graphene field effect transistor.

proximity of graphene's surface molecules, there is change and alterations in the intrinsic electronic structure of the sensing material. In our case, the sensing material graphene is a material of augmented surface area (theoretical surface area of 2630 m²/gm). Such a huge surface area makes graphene an ideal candidate for functionalization with several functional groups for making the humidity sensors sensitive and much more robust. It is usually noticed that gases like CO, H₂, SO₂, H₂S, NH₃, NO, NO₂ and ethanol can be detected in a sensitive manner owing to the gaseous molecular interaction between the exposed gaseous molecules and the graphene sensing material [27].

4.2 Resistive humidity sensors

Resistive humidity sensing has become one of the widest used humidity sensing platforms because of its intrinsic low driven power, easy miniaturization, higher rate of reusability and simplicity in operation and that too at the economical scale. In general, the change in humidity sensing is based on the net change in the electrical resistance of the graphene sensing material, which gets changed with the adsorbing water molecules over the sensing material (**Figure 2**). The configuration of the typical resistive sensor is based on the two conductive electrodes placed on an inert substrate, which besides the resistance change for humidity change can detect the net current change of the sensing mechanism. In order to augment the sensing area of the material, the employed electrodes are usually interdigitated. In the underlying principle, the sensing materials can be made further sensitive by coating the sensing materials with different functional groups, making more surface area available for adsorption of exposed water molecules, making porous structure, compositing the sensitive materials with other available more sensitive components. In this category of sensors, different gaseous analytes like CO, H₂, NO₂, Cl₂, O₂ and other organic vapors can be detected by changing the different sensing materials [28–30].

4.3 Capacitive based humidity sensors

Humidity sensors based upon capacitive properties of the GO materials lies in the fact that GO based sensing materials are insulating in nature. It is seen that

with the available water molecules adsorbed over the GO structure, there is a proportional increase in the proton conductivity rate. This phenomenon signifies the rate of water detection over the structure of GO when tested using capacitive mode. Upon water molecule adsorption, there is proton conductivity which results into change in the capacitance value [31]. In this view it could be argued that GO based capacitive sensors, typically works as water-sensitive dielectric in a purely double-layered electrochemical capacitor for the slightest detection of the humidity available in the surrounding atmosphere. In the configuration side, capacitive based humidity sensors possess the in-plane type to expose the maximum active surface area and is consists of two portions, GO-based sensing materials as the dielectrics and the interdigitated conductive electrodes [32]. In the underlying architecture of the capacitive based humidity sensors, the interdigitated conductive electrodes can be made up of metal materials, as well as rGO based coating for all humidity-based sensing approach. In order to make the sensing material of GO a dielectric based humidity sensing, GO can be composited with the different proton conductive material for making the GO based capacitive based humidity sensing sensitive and robust in nature.

4.4 Surface acoustic wave (SAW) based humidity sensors

The Surface Acoustic Wave (SAW) humidity sensors are basically micro-electromechanical systems, whose detection of humidity is solely based upon the modulation of the surface acoustic waves. Typically, a SAW based humidity sensor comprises of a decay line in between the two interdigitated transducer (IDT), piezoelectric substrate [33]. Mechanical SAW is produced with the input IDT signal under the sinusoidal electrical signal, which uses the net piezoelectric effect of the utilized piezoelectric substrate. The surrounding humidity environment influences the obtained SAW signal. Electrical signal is thus been produced by the available SAW signal by the piezoelectric effect. It is perceived that the changing signals of the amplitude, phase, frequency or time delay could be associated with the occurrence in the sensing phenomenon. The change in the physical properties of the sensing materials like mass, visco-elasticity, conductance also affects the acoustic wave velocity or the net attenuation [34]. It is understood that graphene-based SAW detection of humidity sensing lies in the underlying principle that hydrophilic GO or GO based composites makes the mass dependence SAW signaling of humidity detection. The GO and GO based sensing material consist of defects, which entrap the water molecules for making the mass dependence of SAW, contributing to sensing phenomenon of humidity sensors. It has been investigated by Balashov et al., by preparing a type of humidity sensors by coating a submicron-thick film of GO or a PVA thin film on the decay line, and the same GO based humidity sensor exhibits a sensitivity of 1.54 kHz/ % RH, which is much higher than the 0.47 KHz/% RH and 0.13 KHz/ % RH for the PVA coated and uncoated one [33]. A higher sensitivity from 0.5% RH to 85% RH has been shown by few studies, whereby ZnO piezoelectric thin film has been grown on the glass substrate with GO as the sensing material and layer. The set-up has showed the fastest response (from rise time 1 s and fall time of ~19 s) [35]. Subsequent studies have also revealed that flexible SAW humidity sensors with a different substrate material of polyamide substrate [36]. There are also reports whereby SAW humidity sensors were designed based on the GO film/ ZnO/Si substrate. The set up leads to achieved sensitivity of ~91 KHz/% RH with a net linear response towards humidity sensing in the working range of 20–98% [37]. Another study has revealed that AlN/Si doped layered structure work as SAW humidity sensor, whereby GO has been used as the base sensing material along with the low temperature coefficient of frequency. The value of 42.08 KHz/% RH in RH

higher than 80% has worked excellent at both the lower value of 90% RH humidity showing an improved thermal stability and outstanding short-term repeatability.

4.5 Optical fiber-based humidity sensors

Optical fiber-based humidity sensors work on the principle of sensing humidity inside the optical fiber which gets sensed by deflecting the water molecules inside the optical fibers, dielectric power or the refractive index. As compared to the conventional electronic humidity sensors, such types of sensors have an added advantage of working in the harsher environments, which comprises the flammable environments, higher temperature and electromagnetic immunity. Also, it has been studied that owing to the higher cost of fabrication repeatability, higher cost of optical equipment's has resulted into the limitations in the applications of optical fiber-based humidity sensors. Owing to the excellent water-adsorbing properties of the GO films, graphene materials have been selected as the potential candidate for the humidity sensing inside the optical fiber which has become the best platform for preserving data loss and accurate humidity sensing paradigm. A power variation of up to 6.9 dB in the higher relative humidity range (70–95%) has been achieved by Xiao et al. who have shown the RGO coated side-polished fiber. Such study has shown a correlation efficiency of ~98.2%, a sensitivity of 0.31 dB/% RH, a response speed of faster than 0.13% RH/s with an overall good rate of repeatability in the 75–95% RH [38].

They have shown that the humidity sensor-based on side-polished single mode fiber coated with GO films, resulted into higher and better performance. The polymer channel waveguide upon subsection of the TE mode adsorption at 1550 nm gets influenced by the water molecular adsorption over the surface of GO, which contributes to the linkage between the optical absorption and the net relative humidity mechanism. One of the research studies have shown that Bragg grating coated GO films exhibited a maximum humidity response with sensitivity ~0.129 dB/ % RH which consists a linear coefficient of 99% proportion under the range of 10–80%. This is further dependent upon the water molecular adsorption and desorption phenomenon over the GO films. It has been also shown by them that the optical fiber humidity sensors based on in-fiber Mach-Zehnder interferometer coated with GO or GO/PVA composite shows linearity and good stability [39]. Several studies have highlighted the deposition of Fabry-Perot resonator humidity sensors which is shown by depositing the RGO films or graphene quantum dots [40, 41] over the surface of the hollow core fiber, along with slight leakage of resonant wavelength. Refractive index of the material plays a paramount role in determining the type of RGO based optical sensor in this case. It has been studied that optical fibers coated with the graphene-based materials not only has been used in the humidity sensors but also been used in the biological and chemical sensors.

5. Different graphene-based materials for humidity sensing

It is well known that the molecules of water present in the environment ensures electronic and physical changes in the sensing materials based on graphene. It is noted that by monitoring different property changes such as resistance, mass, surface acoustic wave, capacitance and impedance, detection of humidity is possible. The current section elaborates recent trends in humidity sensors based on graphene. The following section describes sensors based on electronic properties utilizing technique of measurement such as resistance, capacitance and impedance. Six sub classes of graphene-based material are studied in the following section.

5.1 Pristine graphene-based humidity sensor

FET based gas sensor with pristine graphene as sensing material was first demonstrated by Novoselov et al. Micromechanical cleavage of graphite led to formation of pristine graphene which was transferred to the surface of oxidized wafers of silicon. This layer of graphene not only responded to water molecules but also detected presence of ammonia and oxides of carbon and nitrogen [26]. The electronic properties of the gas sensor induce separate responses towards different gases, like ammonia and carbon monoxide act as donors whereas nitrogen dioxide and humidity act as acceptors. Exceptional high sensitivity of graphene-based sensors is achieved due to extremely low noise of graphene. The electronic property of graphene such as band gap varies with change in humidity environment. The band gap is seen to increase with increase in humidity due to increase in adsorbed water molecules on the surface of graphene. This leads to increase in resistivity with increase in humidity [42]. Smith et al. fabricated graphene by CVD process over silicon dioxide and demonstrated an efficient humidity sensor based on resistance change mechanism. The sensor showed fast response and recovery of less than 1 sec due to quick physisorption and desorption of water vapor over the surface of graphene. Simulation showed that the interaction of impurity bands of the substrate with the electrostatic dipole moment of the water molecules leads to sensitivity of the graphene surface to humidity. Popov et al. reported an interesting phenomenon that the adsorption of water molecules at different locations lead to variable resistance change due to divergent mechanism of interaction. An increase in resistivity is observed when the water molecules are adsorbed at the grain boundary defects which occurs due to the p-type nature of graphene and donor type behavior of the water molecules. However, adsorption of water molecules at the edge defects of multilayer graphene contributes to ionic conductivity due to formation of conductive chains. A study by Son et al. revealed that the humidity sensing performance hardly undergoes a change due to physical defects whereas chemical defects may contribute to enhancement in performance. This can be achieved by thickness control of the graphene layer and the area of coverage with PMMA over the graphene surface [43].

A bi-layer graphene-based gas sensor was developed by Fan et al. [44], and its investigation showed a quick humidity response and recovery of the sensor. Experimental calculations supported by theoretical analysis showed that the response of bi-layer graphene was less compared to single layer graphene. Zhu et al. developed a highly efficient humidity sensor, however the sensing material used was wrinkled graphene [45]. The wrinkles prevented aggregation of water molecules (microdroplets) over the graphene surface which facilitated fast desorption leading to quick recovery. The sensor is observed to show ultrafast response of 12.5 ms and can be utilized in monitoring sudden respiratory rate and depth changes. CVD grown graphene over woven fabrics was also developed which was used to detect humidity and temperature simultaneously. A study [46] revealed that interlayer interaction of graphene gets modified when the humidity is over 50%. This calls for further attention to stability and recoverability of multi-layer graphene along with focus on repeatability of the sensor. Hence, even with quick response and recovery, the stability and sensitivity of pristine graphene is an area of improvement.

5.2 Graphene oxide-based humidity sensor

Large scalability, very low cost, high yield, simple preparation technique and high sensitivity to proton-conductivity has encouraged investigation of humidity

sensors based on graphene oxide (GO). The proton conductivity helps in detection of water molecules through impedance or capacitance signals [47]. A humidity sensor was constructed by Bi et al. where they deposited GO over interdigitated micro-electrodes and measured the change in capacitance with a LCR meter. The change in capacitance was observed with change in humidity levels and it also varied with frequency. The sensitivity of the device was found to be high in the RH range 15–95%. The sensor exhibited a response time of 10.5 sec and recovery time of 41 sec. Park et al. demonstrated the relation between adsorption/desorption hysteresis with sensitivity [48] of GO film working in conductometric mode. The study revealed that sensors fabricated at pH 3.3 shows reduced sensitivity and less hysteresis error than the sensors fabricated at pH 9.5. Many strategies are taken up to improve the humidity sensing performance of the GO films such as ultra-large size of GO to enhance the proton conductivity, doping of GO with heteroatoms, GO foams that are free standing facilitating increase in active sites, GO coated over silk fiber to benefit flexibility of the sensor and many more. Graphene oxide may be coated over a flexible substrate to function as a wearable colorimetric humidity sensor as demonstrated by Hong et al. [49].

In general, interdigitated electrodes are prepared by photolithography to contain the GO sensing layer for humidity sensing application. However, gold and silver are quite expensive and patterning requires expensive instruments, skilled professionals and complex procedures. Nowadays, direct laser writing techniques are used to develop electrodes in non-contact mode, with no need for post processing, clean room and are very compatible with commercial electronic product lines such as sensors, devices for energy storage and self-powered devices [50]. Laser irradiation may be used to reduce graphene oxide to form conductive electrodes of reduced graphene oxide with very high conductivity. However, graphene oxide may still act as humidity sensitive sensing layer in the same device. Ajayan et al. developed a micro-supercapacitor (interdigitated) over a hydrated graphene oxide film and demonstrated that proton conductivity in graphene oxide is directly dependent on humidity concentration. A facile fabrication of humidity sensor based on rGO/GO/rGO was reported over a flexible substrate of PET, which used direct laser writing with semiconductor diode laser. The black color of GO turned to gray rGO when laser was irradiated over the GO surface with evolution of certain gases. The rGO so formed was characterized by Raman spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The performance of GO based humidity sensors when evaluated shows very fast response and high sensitivity along with long term stability. Recently, an ultrasensitive humidity sensor have been achieved by Zhang et al. [51] by incorporating polydopamine with graphene oxide and using the principles of quartz crystal microbalance. However, GO based sensors show changes due to proton conductivity, hence their selectivity may be distributed over gases donating or accepting protons. Therefore, selectivity is an area of concern and improvement.

5.3 Reduced graphene oxide-based humidity sensor

The reduction of insulating GO leads to formation of conductive rGO (reduced graphene oxide). The reduced rGO is sensitive to humidity owing to several defects and oxygen containing functional groups in the rGO surface. Incomplete reduction of GO leads to some capacitive behavior of the rGO based sensor. Guo et al. developed graphene oxide over PET substrate by simultaneous reduction and patterning with the help of two-beam-laser interference method [52]. The sensor fabricated showed quick response and recovery with very high sensitivity due to enhanced adsorption of water molecules facilitated by laser induced graphene surface. GO film fabricated through layer-by-layer covalent anchoring showed high sensitivity

in the range 30–90% humidity with minimum hysteresis. The sensor exhibited response time of 28 s and recovery of 48 s with long duration stability [53]. Rapid thermal annealing was carried out on GO by Phan et al. to study the influence of oxygen functional groups on humidity sensing performance [54]. It gives an idea of the sensing properties varying with reduction degree of GO. The work showed that with increase in annealing temperature, GO exhibited reduction in resistivity and led to loss of its capability towards adsorbing water molecules, which ultimately led to reduction in the response of the sensor. A recent study by Shojaei et al. showed that there is variation in sensing performance with degree of reduction of the GO film. They reduced GO by hydrothermal method and the reaction time accounted for the degree of reduction [55]. They found that moderate reduction of GO accounted for optimized sensitivity with response and recovery time. This is because restoration of the sp² carbon network contributes to the response time whereas the residual oxygen groups lead to the sensitivity of the GO film. A study by Papazoglou et al. elaborated on the reduction of GO by laser reduction and in-situ sequential laser transfer. The sensor exhibited a response time of less than one minute in water concentration 1700–20000 ppm having 1700 ppm as limit of detection [56].

Humidity sensing being a significant part of our daily life, rGO based flexible and wearable sensors have attracted much attention. Preparation of rGO based sensors in fiber substrate is one of the many strategies to make wearable sensor devices. Qu's group fabricated microfibers based on double helix core sheath rGO which was sensitive to multiple stimulus. Small changes in temperature, mechanical properties and RH led to significant current response [57]. A unique humidity sensor was fabricated by Choi et al. where the sensing layer was nitrogen doped rGO fibers with platinum nanoparticles deposited on the rGO surface. These nanoparticles behaved as dissociation catalysts while sensing humidity. A wide range of humidity (6.1–66.4%) was detected by the rGO fibers with 136% sensitivity. Wearable devices based on natural fibers such as silk or spider silk are employed to achieve biodegradability, superior mechanical properties and excellent skin affinity. A flexible humidity sensor was fabricated by Li et al. where silk fabrics were coated with nickel and GO sheets. The sensor exhibited very fast detection towards humidity and showed probable use in monitoring human respiration [58]. Silk interlayers were introduced into GO films by Ma et al. who proposed a very light weight and tough printable bio papers for humidity sensing applications [59].

5.4 Graphene/2D materials-based humidity sensor

Recently, ultrasensitive sensors based on 2D materials such as TMDCs (transition metal dichalcogenides) like WS₂ and MoS₂ and black phosphorus have gained significant attention owing to their novel electronic properties and structures. Graphene has been incorporated with WS₂, MoS₂ and black phosphorus as nanocomposites for enhanced performance as humidity sensors. The first humidity sensor based on MoS₂/GO was developed by Burman et al. which exhibited extremely high response of 1600 times at 85% RH. This high response was due to enhanced proton conductivity in MoS₂ and GO [60]. Another work based on MoS₂/rGO composites were reported by Park et al., where they prepared the composites without any additional heating or additives. Then the composite material was drop casted over interdigitated electrodes for sensing humidity [61]. The MoS₂/rGO composites exhibited 200 times enhanced response towards water molecules when compared to pure rGO based sensor. Formation of a p-n heterojunction between rGO and MoS₂ led to this remarkable improvement in the sensing performance. Hydrothermal method to fabricate rGO/MoS₂ composites for high performance humidity sensor

was developed by Park et al. [62]. Jha et al. developed GO/WS2 composite for sensing humidity exhibiting 65.8 times response at 40% RH and 590 times response at 80% RH. The sensor exhibited a response time of 25 s and a recovery time of 29 s which was due to improved proton conductivity at the GO/WS2 interface due to oxygen linking activities [63]. The 2D layer and crystalline nature of black phosphorus induced water molecules to naturally adsorb onto the surface attributing to ultra-sensitive nature of black phosphorus. However, it suffered from repeatability due to instability of water molecules with black phosphorus. This limitation was overcome by Phan et al. when they developed black phosphorus/graphene composite by introducing graphene into black phosphorus. The stability of the sensor was taken care by the interface formed between graphene and black phosphorus. The sensor showed linearity in response within 15–70% RH with a response of 43.4% at 70% RH. Response time of 9 s and recovery time of 30 s was noted for this composite structure. Humidity sensors based on graphene/2D material shows potential, among which MoS2/rGO composites have maximum potential. However, the response and recovery time of the sensors must be reduced for achieving optimum performance.

5.5 Graphene quantum dots as humidity sensor

Graphene quantum dots (GQDs) exhibits almost similar properties and structure as layered-graphene, however its electronic properties are based upon electronic states at the edge and size of the quantum dots (exhibiting quantum confinement). The size can be controlled to manipulate the desired properties of GQD. Sreeprasad et al. developed a humidity sensor based on percolating network of GQDs which was assembled selectively over a polyelectrolyte microfiber. The work explained electron-tunneling modulation in the network of GQDs. Here GQDs was responsible for electron transportation and the polymer was responsible for water mass transfer [64]. The presence of water vapor reduced the width of tunneling barrier between GQDs by 0.36 nm and enhanced its conductivity 43 times. Ruiz et al. developed a resistive humidity sensor based on GQDs which was prepared by pyrolysis of citric acid over interdigitated electrodes [65]. An exponential variation of sensitivity over the RH range 15–80% was observed along with a quick response of ~5 s. The water molecules condensed over the GQD surface through capillary action which accounted for enhanced sensing performance. A similar approach was taken by Alizadeh et al. to prepare GQD based humidity sensor [66], which showed enormous sensitivity to humidity variation in the environment with response time close to 10 s. Interestingly they reported two separate sensing phenomena for 0–52% RH and 52–97% RH. When the RH range was low, the electrical resistance decreased as the adsorbed water molecules injected hole carriers. However, at the high RH range, the ionic proton transportation improved due to the adsorption of water molecules and caused a reduction in electrical resistance of the sensor. For the first time a flexible humidity sensor based on GQD was demonstrated by Hosseini et al. where a facile hydrothermal method was used to synthesize GQDs. The synthesized GQDs were drop casted on interdigitated electrodes fabricated over a flexible polyimide substrate (**Figure 3(a)**) [66]. The GQD film exhibited porous like structure which enhanced the sensing performance as shown in **Figure 3(b)**. The fabricated sensor exhibited exponential characteristics in response towards 12–100% humidity range. The response and recovery time of the sensor was found to be 12 s and 43 s respectively as depicted in **Figure 3(c)**. The sensor showed a quick response when exposed to human breath flow (90% RH) as shown in **Figure 3(d)**. Hence, it is found that GQDs have certain benefits as humidity sensor such as good selectivity, enhanced response and very fast response

Figure 3.

(a) Schematic of flexible sensor; (b) FESEM image of the sensing material; (c) response vs. RH plot; (d) response to human breath. Reproduced with permission from [66], copyright the Royal Society of Chemistry, 2017.

and recovery. Few more studies on GQDs (especially on stability) can establish it on commercial platform as potential humidity sensor.

5.6 Graphene/metal or graphene/metal oxide as humidity sensor

Humidity sensing performance of metal oxides such as ZnO, SnO₂, CuO was observed due to diversity in morphology, high surface to volume ratio, presence of defects and vacancies. However, limitation was observed in conductivity and they exhibited slow electron diffusion which was responsible for reduced response. On the other hand, GO or rGO exhibited lack of reversibility. Therefore, a graphene/metal oxide composite may enhance the sensing performance optimally.

Humidity sensors based on graphene/ SnO₂ composite has been widely studied, where the humidity sensing performance was observed to improve due to incorporation of graphene over SnO₂. A study on SnO_x coated with graphene on carbon fibers (graphene/SnO_x/CF) [67] exhibited sensitivity of 6.22 which is 2 times higher than the uncoated one [68]. A humidity sensor based on SnO₂/graphene wrapped with GO was developed by Xu et al. which showed very fast response and recovery (less than 1 s) and enormous sensitivity of 32 MΩ/RH%. This high sensitivity and good stability of the sensor was due to enhanced conductivity of graphene and oxygen rich functional groups of GO (specially hydroxyl and epoxy). A one step facile hydrothermal method was used to fabricate rGO/SnO₂ composite by Zhang et al. The composite material after fabrication was drop casted on microelectrodes for developing the humidity sensor. The sensor exhibited enhanced sensitivity, fast response and recovery when compared to pristine rGO. The improvement in sensitivity was dedicated to the defects and vacancies introduced by SnO₂

Sl. No	Sensing layer	Working principle/Measurement parameters	Reference
1.	Graphene oxide	Capacitive	[32]
2.	Graphene oxide thin film	Surface acoustic wave atomizer	[33]
3.	Graphene oxide	Optical fiber	[39]
4.	Graphene	Field effect transistor	[27]
5.	SnS2-Reduced graphene oxide	Resistive	[29]
6.	Graphene	Resistive	[42]
7.	Polydopamine/ graphene oxide	Quartz crystal microbalance	[51]
8.	Graphene quantum dots	Resistive	[65]
9.	Reduced graphene oxide/CuO	Resistive	[70]
10.	Self-powered Graphene oxide	Open circuit voltage and current	[74]

Table 1.
Shows the evolution of graphene-based humidity sensors based upon the sensing layer and the different working principles.

nanoparticles and the interface formed between the two materials. Investigation of the same material as humidity sensor was also carried in resistive mode [69]. Fe doped SnO₂ nanoparticles when employed with rGO sheets displayed highly improved sensing performance [69]. A rGO/CuO nano-composite was synthesized by Wang et al. which showed relatively good sensing characteristics [70]. The sensor showed fast response and high sensitivity which was mainly due the formation of Schottky junction between the two materials. It has been demonstrated that even incorporation of graphene on ZnO or TiO₂ nanoparticles enhance the performance of the humidity sensors [71].

There are few reports on humidity sensors based on composite of graphene and metal nanoparticles. A molecular combing method to prepare GO-Ag scrolls was developed by Liu et al. where the Ag nanoparticles were deposited uniformly over the GO surface [72]. The material when reduced by hydrazine to rGO/Ag scrolls showed a response of 3 orders in magnitude compared to that of bare rGO scrolls when exposed to humid atmosphere. The improvement in conductivity of the rGO/Ag scrolls due to encapsulation of the silver nanoparticles contributed towards excellent sensitivity of the sensor. Conduction pathways formed by Ag nanoparticles on the surface of rGO by self-assembly led to improvement of response and linearity of the sensor device. An interesting work by Yeo et al. showed the suppression of humidity dependence of the sensor based on rGO due to incorporation of Cu nanoparticles. The Cu nanoparticles were used to reduce the electrical resistance to detect various other gases (**Table 1**) [73].

6. Future outlook and summary

Different mechanisms have been attempted to develop highly efficient humidity sensors based on graphene. Pristine graphene-based humidity sensors exhibit high response with 1 ppm detection limit; however, it faces issues such as poor recovery and limited selectivity. The recovery and selectivity limitations can be overcome by chemical modification of the graphene surface with desired functional groups. Humidity sensors based on graphene oxide shows good sensitivity and quick response in the higher range of humidity. However, at low humidity conditions (less than 5%), detection is challenging. At higher humidity levels, these graphene

oxide sensors exhibit relatively poor stability and swelling effect. Complicated circuits are required for impedance or capacitive working mode. Reduced graphene oxide, another counterpart of graphene facilitates development of resistive humidity sensors with very easy methods of fabrication. These sensors consume very less power and are easy to detect. Reduced graphene oxide has lesser number of oxygen functional groups compared to graphene oxide, which leads to reduction in sensing response. Different other approaches such as incorporating graphene with metal nanoparticles, metal oxide nanoparticles or 2D layered materials have enormously improved the sensitivity, range of detection, negligible hysteresis and quick response. However, these devices suffer from long duration stability and reproducibility.

High performance humidity sensors based on graphene is still required with sufficiently high sensitivity, wide range of humidity, high degree of selectivity, quick recovery and response time and negligible hysteresis. The foremost important requirement of the graphene-based sensor is long term stability, repeatability and full recovery. The degree of oxidation and reduction of graphene sheets possess a challenge towards reproducibility of the graphene- based sensors. The formation of graphene oxide and its reduction needs precise control, failing to which leads to different sensing performance. Improvement is also required in terms of detection range of humidity. Sensing at low humidity is also an important parameter. At last, it is very important now to consider issues related to commercialization of graphene- based humidity sensors. The points to be considered are repeatability, long term stability, large scale integration, packaging and anti-chemical characteristics. An industrially manufactured digital biosensor based on graphene is developed by Goldsmith et al. [75], however it has a long way to go towards commercialization. Most of the studies in humidity sensor based on graphene have not considered the issue of power consumption, which is one of the key focus areas while developing wearable electronics.

Acknowledgements

The authors would like to thank Microelectronics and MEMS laboratory, IIT Kharagpur for supporting this work.

IntechOpen

Author details

Avik Sett¹, Kunal Biswas², Santanab Majumder³, Arkaprava Datta³
and Tarun Kanti Bhattacharyya^{1*}

1 Department of Electronics and Electrical Communication Engineering,
IIT Kharagpur, Kharagpur, West Bengal, India

2 Department of Biotechnology, Maulana Abul Kalam Azad University of
Technology, West Bengal, India

3 School of Nanoscience and Technology, IIT Kharagpur, Kharagpur, West Bengal,
India

*Address all correspondence to: tkb@ece.iitkgp.ac.in

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

- [1] Seiyama, T., Yamazoe, N. and Arai, H., 1983. Ceramic humidity sensors. *Sensors and Actuators*, 4, pp.85-96.
- [2] Chen, Z. and Lu, C., 2005. Humidity sensors: A review of materials and mechanisms. *Sensor letters*, 3(4), pp.274-295.
- [3] Blank, T.A., Eksperiandova, L.P. and Belikov, K.N., 2016. Recent trends of ceramic humidity sensors development: A review. *Sensors and Actuators B: Chemical*, 228, pp.416-442.
- [4] Manikandan, V., Sikarwar, S., Yadav, B.C. and Mane, R.S., 2018. Fabrication of tin substituted nickel ferrite (Sn-NiFe₂O₄) thin film and its application as opto-electronic humidity sensor. *Sensors and Actuators A: Physical*, 272, pp.267-273.
- [5] Tripathy, A., Pramanik, S., Manna, A., Bhuyan, S., Azrin Shah, N.F., Radzi, Z. and Abu Osman, N.A., 2016. Design and development for capacitive humidity sensor applications of lead-free Ca, Mg, Fe, Ti-oxides-based electro-ceramics with improved sensing properties via physisorption. *Sensors*, 16(7), p.1135.
- [6] Li, W., Liu, J., Ding, C., Bai, G., Xu, J., Ren, Q. and Li, J., 2017. Fabrication of ordered SnO₂ nanostructures with enhanced humidity sensing performance. *Sensors*, 17(10), p.2392.
- [7] A. Sett, A.K.Mukhopadhyay, Monojit Mondal, Santanab Majumder and T.K.Bhattacharyya, 2018. Tuning surface defects of mesoporous ZnO nanorods for high-speed humidity sensing applications. *IEEE Sensors Conference 2018*.
- [8] Morais, R.M., dos Santos Klem, M., Nogueira, G.L., Gomes, T.C. and Alves, N., 2018. Low cost humidity sensor based on PANI/PEDOT: PSS printed on paper. *IEEE Sensors Journal*, 18(7), pp.2647-2651.
- [9] Zhao, J., Li, N., Yu, H., Wei, Z., Liao, M., Chen, P., Wang, S., Shi, D., Sun, Q. and Zhang, G., 2017. Highly sensitive MoS₂ humidity sensors array for noncontact sensation. *Advanced materials*, 29(34), p.1702076.
- [10] Guo, H., Lan, C., Zhou, Z., Sun, P., Wei, D. and Li, C., 2017. Transparent, flexible, and stretchable WS₂ based humidity sensors for electronic skin. *Nanoscale*, 9(19), pp.6246-6253.
- [11] Cho, S.Y., Lee, Y., Koh, H.J., Jung, H., Kim, J.S., Yoo, H.W., Kim, J. and Jung, H.T., 2016. Superior chemical sensing performance of black phosphorus: Comparison with MoS₂ and graphene. *Advanced Materials*, 28(32), pp.7020-7028.
- [12] Zhou, G., Byun, J.H., Oh, Y., Jung, B.M., Cha, H.J., Seong, D.G., Um, M.K., Hyun, S. and Chou, T.W., 2017. Highly sensitive wearable textile-based humidity sensor made of high-strength, single-walled carbon nanotube/poly (vinyl alcohol) filaments. *ACS applied materials & interfaces*, 9(5), pp.4788-4797.
- [13] Varghese, S.S., Lonkar, S., Singh, K.K., Swaminathan, S. and Abdala, A., 2015. Recent advances in graphene based gas sensors. *Sensors and Actuators B: Chemical*, 218, pp.160-183.
- [14] Yavari, F. and Koratkar, N., 2012. Graphene-based chemical sensors. *The journal of physical chemistry letters*, 3(13), pp.1746-1753.
- [15] Park, S., An, J., Suk, J.W. and Ruoff, R.S., 2010. Graphene-based actuators. *Small*, 6(2), pp.210-212.
- [16] Lee, C., Wei, X., Kysar, J.W. and Hone, J., 2008. Measurement of the

elastic properties and intrinsic strength of monolayer graphene. *Science*, 321(5887), pp.385-388.

[17] Lipson, H.S. and Stokes, A.R., 1942. The structure of graphite. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 181(984), pp.101-105.

[18] Abbott's, I.E., 2007. Graphene: Exploring carbon flatland. *Phys. Today*, 60(8), p.35.

[19] Geim, A.K., 2009. Graphene: Status and prospects. *Science*, 324(5934), pp.1530-1534.

[20] Geim, A.K. and Novoselov, K.S., 2010. The rise of graphene. In *nanoscience and technology: A collection of reviews from nature journals* (pp. 11-19).

[21] Lee, C., Wei, X., Kysar, J.W. and Hone, J., 2008. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 321(5887), pp.385-388.

[22] Chen, J., Yao, B., Li, C. and Shi, G., 2013. An improved hummers method for eco-friendly synthesis of graphene oxide. *Carbon*, 64, pp.225-229.

[23] Chaste, J., Saadani, A., Jaffre, A., Madouri, A., Alvarez, J., Pierucci, D., Aziza, Z.B. and Ouerghi, A., 2017. Nanostructures in suspended mono-and bilayer epitaxial graphene. *Carbon*, 125, pp.162-167.

[24] Fogarassy, Z., Rummeli, M.H., Gorantla, S., Bachmatiuk, A., Dobrik, G., Kamarás, K., Biró, L.P., Havancsák, K. and Lábár, J.L., 2014. Dominantly epitaxial growth of graphene on Ni (1 1 1) substrate. *Applied surface science*, 314, pp.490-499.

[25] Tetlow, H., De Boer, J.P., Ford, I.J., Vvedensky, D.D., Coraux, J. and Kantorovich, L., 2014. Growth of

epitaxial graphene: Theory and experiment. *Physics reports*, 542(3), pp.195-295.

[26] Schedin, F., Geim, A.K., Morozov, S.V., Hill, E.W., Blake, P., Katsnelson, M.I. and Novoselov, K.S., 2007. Detection of individual gas molecules adsorbed on graphene. *Nature materials*, 6(9), pp.652-655.

[27] He, Q., Wu, S., Yin, Z. and Zhang, H., 2012. Graphene-based electronic sensors. *Chemical Science*, 3(6), pp.1764-1772.

[28] Meng, F.L., Guo, Z. and Huang, X.J., 2015. Graphene-based hybrids for chemiresistive gas sensors. *TrAC Trends in Analytical Chemistry*, 68, pp.37-47.

[29] Shafiei, M., Bradford, J., Khan, H., Piloto, C., Wlodarski, W., Li, Y. and Motta, N., 2018. Low-operating temperature NO₂ gas sensors based on hybrid two-dimensional SnS₂-reduced graphene oxide. *Applied Surface Science*, 462, pp.330-336.

[30] Piloto, C., Shafiei, M., Khan, H., Gupta, B., Tesfamichael, T. and Motta, N., 2018. Sensing performance of reduced graphene oxide-Fe doped WO₃ hybrids to NO₂ and humidity at room temperature. *Applied Surface Science*, 434, pp.126-133.

[31] Gao, W., Singh, N., Song, L., Liu, Z., Reddy, A.L.M., Ci, L., Vajtai, R., Zhang, Q., Wei, B. and Ajayan, P.M., 2011. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nature nanotechnology*, 6(8), pp.496-500.

[32] Bi, H., Yin, K., Xie, X., Ji, J., Wan, S., Sun, L., Terrones, M. and Dresselhaus, M.S., 2013. Ultrahigh humidity sensitivity of graphene oxide. *Scientific reports*, 3(1), pp.1-7.

[33] Balashov, S.M. and Balachova, O.V., 2012. Filho, AP; Bazetto, MCQ; de

Almeida, MG surface acoustic wave humidity sensors based on graphene oxide thin films deposited with the surface acoustic wave atomizer. ECS Trans, 49, pp.445-450.

[34] Wohltjen, H., 1984. Mechanism of operation and design considerations for surface acoustic wave device vapour sensors. Sensors and Actuators, 5(4), pp.307-325.

[35] Xuan, W., He, M., Meng, N., He, X., Wang, W., Chen, J., Shi, T., Hasan, T., Xu, Z., Xu, Y. and Luo, J.K., 2014. Fast response and high sensitivity ZnO/glass surface acoustic wave humidity sensors using graphene oxide sensing layer. Scientific reports, 4(1), pp.1-9.

[36] Xuan, W., He, X., Chen, J., Wang, W., Wang, X., Xu, Y., Xu, Z., Fu, Y.Q. and Luo, J.K., 2015. High sensitivity flexible lamb-wave humidity sensors with a graphene oxide sensing layer. Nanoscale, 7(16), pp.7430-7436.

[37] Kuznetsova, I.E., Anisimkin, V.I., Kolesov, V.V., Kashin, V.V., Osipenko, V.A., Gubin, S.P., Tkachev, S.V., Verona, E., Sun, S. and Kuznetsova, A.S., 2018. Sezawa wave acoustic humidity sensor based on graphene oxide sensitive film with enhanced sensitivity. Sensors and Actuators B: Chemical, 272, pp.236-242.

[38] Xiao, Y., Zhang, J., Cai, X., Tan, S., Yu, J., Lu, H., Luo, Y., Liao, G., Li, S., Tang, J. and Chen, Z., 2014. Reduced graphene oxide for fiber-optic humidity sensing. Optics express, 22(25), pp.31555-31567.

[39] Wang, Y., Shen, C., Lou, W. and Shentu, F., 2016. Polarization-dependent humidity sensor based on an in-fiber Mach-Zehnder interferometer coated with graphene oxide. Sensors and Actuators B: Chemical, 234, pp.503-509.

[40] Wang, Ning, Wenhao Tian, Haosheng Zhang, Xiaodan Yu, Xiaolei

Yin, Yonggang Du, and Dailin Li. "An easily fabricated high performance Fabry-Perot optical fiber humidity sensor filled with graphene quantum dots." Sensors 21, no. 3 (2021): 806.

[41] Owji, Erfan, Hossein Mokhtari, Fatemeh Ostovari, Behnam Darazereshki, and Nazanin Shakiba. "2D materials coated on etched optical fibers as humidity sensor." Scientific Reports 11, no. 1 (2021): 1-10.

[42] Yavari, F., Kritzing, C., Gaire, C., Song, L., Gulapalli, H., Borca-Tasciuc, T., Ajayan, P.M. and Koratkar, N., 2010. Tunable bandgap in graphene by the controlled adsorption of water molecules. Small, 6(22), pp.2535-2538.

[43] Son, Y.J., Chun, K.Y., Kim, J.S., Lee, J.H. and Han, C.S., 2017. Effects of chemical and physical defects on the humidity sensitivity of graphene surface. Chemical Physics Letters, 689, pp.206-211.

[44] Fan, X., Elgammal, K., Smith, A.D., Östling, M., Delin, A., Lemme, M.C. and Niklaus, F., 2018. Humidity and CO₂ gas sensing properties of double-layer graphene. Carbon, 127, pp.576-587.

[45] Zhen, Z., Li, Z., Zhao, X., Zhong, Y., Zhang, L., Chen, Q., Yang, T. and Zhu, H., 2018. Formation of uniform water microdroplets on wrinkled graphene for ultrafast humidity sensing. Small, 14(15), p.1703848

[46] Qadir, A., Sun, Y.W., Liu, W., Oppenheimer, P.G., Xu, Y., Humphreys, C.J. and Dunstan, D.J., 2019. Effect of humidity on the interlayer interaction of bilayer graphene. Physical review B, 99(4), p.045402.

[47] Yao, Y., Chen, X., Zhu, J., Zeng, B., Wu, Z. and Li, X., 2012. The effect of ambient humidity on the electrical properties of graphene oxide films. Nanoscale research letters, 7(1), pp.1-7.

- [48] Park, E.U., Choi, B.I., Kim, J.C., Woo, S.B., Kim, Y.G., Choi, Y. and Lee, S.W., 2018. Correlation between the sensitivity and the hysteresis of humidity sensors based on graphene oxides. *Sensors and Actuators B: Chemical*, 258, pp.255-262.
- [49] Chi, Hong, Lim Jun Ze, Xuemin Zhou, and Fuke Wang. "GO film on flexible substrate: An approach to wearable colorimetric humidity sensor." *Dyes and Pigments* 185 (2021): 108916
- [50] Cai, J., Lv, C. and Watanabe, A., 2016. Laser direct writing of high-performance flexible all-solid-state carbon micro-supercapacitors for an on-chip self-powered photodetection system. *Nano Energy*, 30, pp.790-800.
- [51] Zhang, Dongzhi, Xiaoshuang Song, Zhao Wang, and Haonan Chen. "Ultra-highly sensitive humidity sensing by polydopamine/graphene oxide nanostructure on quartz crystal microbalance." *Applied Surface Science* 538 (2021): 147816.
- [52] Guo, L., Jiang, H.B., Shao, R.Q., Zhang, Y.L., Xie, S.Y., Wang, J.N., Li, X.B., Jiang, F., Chen, Q.D., Zhang, T. and Sun, H.B., 2012. Two-beam-laser interference mediated reduction, patterning and nanostructuring of graphene oxide for the production of a flexible humidity sensing device. *Carbon*, 50(4), pp.1667-1673.
- [53] Su, P.G. and Chiou, C.F., 2014. Electrical and humidity-sensing properties of reduced graphene oxide thin film fabricated by layer-by-layer with covalent anchoring on flexible substrate. *Sensors and Actuators B: Chemical*, 200, pp.9-18.
- [54] Phan, D.T. and Chung, G.S., 2015. Effects of rapid thermal annealing on humidity sensor based on graphene oxide thin films. *Sensors and Actuators B: Chemical*, 220, pp.1050-1055.
- [55] Shojaei, M.H.S.M., Nasresfahani, S., Dordane, M.K. and Sheikhi, M.H., 2018. Fully integrated wearable humidity sensor based on hydrothermally synthesized partially reduced graphene oxide. *Sensors and Actuators A: Physical*, 279, pp.448-456.
- [56] Papazoglou, S., Petridis, C., Kymakis, E., Kennou, S., Raptis, Y.S., Chatzandroulis, S. and Zergioti, I., 2018. In-situ sequential laser transfer and laser reduction of graphene oxide films. *Applied physics letters*, 112(18), p.183301.
- [57] Zhao, F., Zhao, Y., Cheng, H. and Qu, L., 2015. A graphene fibriform responsor for sensing heat, humidity, and mechanical changes. *Angewandte Chemie*, 127(49), pp.15164-15168.
- [58] Li, B., Xiao, G., Liu, F., Qiao, Y., Li, C.M. and Lu, Z., 2018. A flexible humidity sensor based on silk fabrics for human respiration monitoring. *Journal of Materials Chemistry C*, 6(16), pp.4549-4554.
- [59] Ma, R. and Tsukruk, V.V., 2017. Serigraphy-guided reduction of graphene oxide biopapers for wearable sensory electronics. *Advanced functional materials*, 27(10), p.1604802.
- [60] Burman, D., Ghosh, R., Santra, S. and Guha, P.K., 2016. Highly proton conducting MoS₂/graphene oxide nanocomposite based chemoresistive humidity sensor. *Rsc Advances*, 6(62), pp.57424-57433.
- [61] Park, S.Y., Kim, Y.H., Lee, S.Y., Sohn, W., Lee, J.E., Shim, Y.S., Kwon, K.C., Choi, K.S., Yoo, H.J., Suh, J.M. and Ko, M., 2018. Highly selective and sensitive chemoresistive humidity sensors based on rGO/MoS₂ van der Waals composites. *Journal of Materials Chemistry A*, 6(12), pp.5016-5024.
- [62] Park, S.Y., Lee, J.E., Kim, Y.H., Kim, J.J., Shim, Y.S., Kim, S.Y., Lee, M.H. and

- Jang, H.W., 2018. Room temperature humidity sensors based on rGO/MoS₂ hybrid composites synthesized by hydrothermal method. *Sensors and Actuators B: Chemical*, 258, pp.775-782.
- [63] Jha, R.K., Burman, D., Santra, S. and Guha, P.K., 2017. WS₂/GO nanohybrids for enhanced relative humidity sensing at room temperature. *IEEE Sensors Journal*, 17(22), pp.7340-7347.
- [64] Sreeprasad, T.S., Rodriguez, A.A., Colston, J., Graham, A., Shishkin, E., Pallem, V. and Berry, V., 2013. Electron-tunneling modulation in percolating network of graphene quantum dots: Fabrication, phenomenological understanding, and humidity/pressure sensing applications. *Nano letters*, 13(4), pp.1757-1763.
- [65] Ruiz, V., Fernández, I., Carrasco, P., Cabañero, G., Grande, H.J. and Herrán, J., 2015. Graphene quantum dots as a novel sensing material for low-cost resistive and fast-response humidity sensors. *Sensors and Actuators B: Chemical*, 218, pp.73-77.
- [66] Hosseini, Z.S., Ghiass, M.A., Fardindoost, S. and Hatamie, S., 2017. A new approach to flexible humidity sensors using graphene quantum dots. *Journal of Materials Chemistry C*, 5(35), pp.8966-8973.
- [67] Xu, J., Gu, S. and Lu, B., 2015. Graphene and graphene oxide double decorated SnO₂ nanofibers with enhanced humidity sensing performance. *RSC advances*, 5(88), pp.72046-72050.
- [68] Fu, T., Zhu, J., Zhuo, M., Guan, B., Li, J., Xu, Z. and Li, Q., 2014. Xu, J., Gu, S. and Lu, B., 2015. Graphene and graphene oxide double decorated SnO₂ nanofibers with enhanced humidity sensing performance. *RSC advances*, 5(88), pp.72046-72050. *Journal of Materials Chemistry C*, 2(24), pp.4861-4866.
- [69] Zhang, D., Chang, H. and Liu, R., 2016. Humidity-sensing properties of one-step hydrothermally synthesized tin dioxide-decorated graphene nanocomposite on polyimide substrate. *Journal of Electronic Materials*, 45(8), pp.4275-4281.
- [70] Toloman, D., Popa, A., Stan, M., Socaci, C., Biris, A.R., Katona, G., Tudorache, F., Petrila, I. and Iacomi, F., 2017. Reduced graphene oxide decorated with Fe doped SnO₂ nanoparticles for humidity sensor. *Applied Surface Science*, 402, pp.410-417.
- [71] Wang, Z., Xiao, Y., Cui, X., Cheng, P., Wang, B., Gao, Y., Li, X., Yang, T., Zhang, T. and Lu, G., 2014. Humidity-sensing properties of urchinlike CuO nanostructures modified by reduced graphene oxide. *ACS applied materials & interfaces*, 6(6), pp.3888-3895.
- [72] Liu, Y., Wang, L., Zhang, H., Ran, F., Yang, P. and Li, H., 2017. Graphene oxide scroll meshes encapsulated Ag nanoparticles for humidity sensing. *RSC advances*, 7(64), pp.40119-40123.
- [73] Yeo, C.S., Kim, H., Lim, T., Kim, H.J., Cho, S., Cho, K.R., Kim, Y.S., Shin, M.K., Yoo, J., Ju, S. and Park, S.Y., 2017. Copper-embedded reduced graphene oxide fibers for multi-sensors. *Journal of Materials Chemistry C*, 5(48), pp.12825-12832.
- [74] Ejehi, Faezeh, Raheleh Mohammadpour, Elham Asadian, Pezhman Sasanpour, Somayeh Fardindoost, and Omid Akhavan. "Graphene oxide papers in nanogenerators for self-powered humidity sensing by finger tapping." *Scientific reports* 10, no. 1 (2020): 1-11.
- [75] Goldsmith, B.R., Locascio, L., Gao, Y., Lerner, M., Walker, A., Lerner, J., Kyaw, J., Shue, A., Afsahi, S., Pan, D. and Nokes, J., 2019. Digital biosensing by foundry-fabricated graphene sensors. *Scientific reports*, 9(1), pp.1-10.