Contemporary Advances in Humidity Sensing Materials, Methods, and Performances

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The present review paper describes the advances in materials, mechanisms, and techniques for humidity sensing along with their applications in terms of parameters, utility, durability, and spectrum. Advances in different types of humidity sensing materials are described along with their processing techniques, significance in humidity sensing properties, and applications. The newer application for the use of humidity sensors i.e. monitoring of respiration, metabolic rate, quality of organic solvents, packaging, power plants, agriculture practices, and forensic cases was also explained with suitable illustrations and current references. Although humidity sensing is a very old analytical tool but still suffers from several challenges for appropriate applications. In conclusion, a road map for the nexus between materials science, technology, applications, and existing challenges are presented about humidity sensors.

Introduction

Synchronized advances in material science, analytical principle, and data processing have been drastically improved the humidity sensing technology with a prolonged horizon of its applications from the monitoring of the environment to physiological conditions in humans. Although, humidity sensing is an ancient sensing technology for monitoring of atmospheric conditions by human as well as by natural changes like the opening of leaves of pinecone at specified range humidity to release their spores for fertilisations and discomforts in humans at high humidity [**1**]. But, the current analytical progress in the analytical advances has attracted significant interest in chemists, physicists, and engineers to design efficient and effective humidity sensors after exploiting the wide range of materials i.e. minerals, ceramics, polymers, and carbon nanostructures in extended prospect with better parameters [**2**]. Furthermore, the blending of materials with size and dimension confinements is another breadth in advancing the sensing of humidity saturate to trace level in solid, liquid, and gaseous state [**3**].

In this context, several transducers are used for humidity monitoring after using different materials like ceramic, polymers, carbon nanostructure, and organo-metallic compounds. These advances in humidity sensors are revealing their prospects in atmospheric sciences, food packaging, biomedical, agriculture, and human comforts with several limitations [**4**]. In course of scientific progress has been witnessed with consistent publications in research articles, book chapters, and reviews. A pictorial representation in the trend of publications of humidity sensors has been depicted in **Fig. 1** and the theme of important reviews are listed in **Table 1** based on the Scopus search on search title humidity sensors on 28.11.20 at Indian time 8.30 p.m.

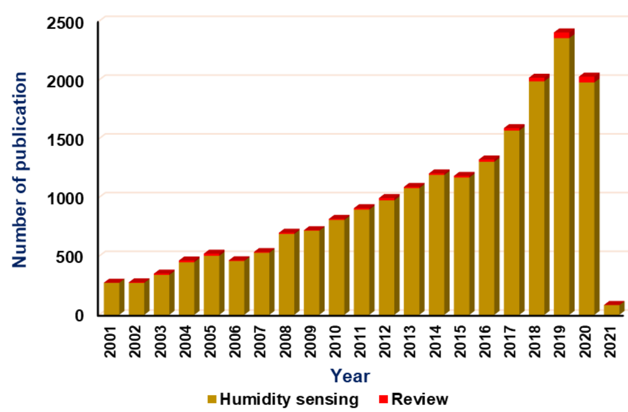

Fig. 1. The trend in year wise publication in humidity sensors. (www.scopus.com).

The search is revealing a total of 22123 manuscripts are published, which includes 344 reviews on the topic. The summary of existing literature on the topic is indicating that the synergized report between materials, methods, and applications is the demand of current progress in humidity sensing research for a researcher to understand the updated picture on the topic. In line with the above discussions, the present review articles present the advances in humidity sensing materials, sensing mechanisms, and technologies along with their role in advancement in exiting humidity sensors. The importance of techniques has witnessed for the consistent increasing rate of publications, which creates a challenge to select the research paper to include in this paper this is possible that some paper may eliminate from this review. However, an honest attempt has been made to select the papers on the basis of their impact on humidity sensing and their novelty.

Table 1. Important reviews on the humidity sensor with their objectives

S. N.	Materials	Aim	Brief description	References
1	Silicon-based detectors	High-energy physics applications	Humidity sensing and radiation effects on the sensing materials	5
2	Paper-Based Sensors	Design principle	Fabrications of electrodes, sensing materials, and applications	6
3	Optical Fiber(OF)	Technologies, pros, and cons	High-end technology with desired specifications and challenge	7
4	Flexible conductive materials	Packaging applications	Resistive humidity sensing applications and parameters	8
5	Microfiber knot resonators	Humidity sensors	Change in resonant wavelength and the transmission output due to surface interaction of water molecules.	9
6.	Organic thin-film	Resistive and Capacitive Humidity Sensors	Fundamental working principles, designs, and characterization	10
7	Microphone sensors	Radio Frequency identification system	Sensing of leakage from pipelines employing low-power wireless sensors based external devices and mobile robot	11
8	Ceramic	Basic principle of ceramic-based humidity sensors	Advanced practices for preparing ceramic-based humidity sensors along with key finding and challenges	12
9.	Organic and inorganic functional materials	Significant issues in humidity sensing	State of the art humidity sensor types, principles, sensing substances, mechanisms, and production	13
10	Polymers, Ceramic, and semiconductors	Electrical properties of humidity sensors	Preparation and characterization of sensing materials and their applications	14
11	Semiconductors	Semiconductor technology	Highly accurate humidity sensors with resistance to chemicals and physical contaminants	15
12	Ceramic, polymer, and carbon nanostructure	Contemporary advances	Advances in materials, mechanism, and techniques with parameters and challenges	Present works

Overview of the humidity sensor

The presence of water molecules (H_2O) is a significant driving force for the progress of physical, chemical, and biological processes. In nature the water alone chemical compound, which simultaneously exists in all three-form solid (ice), liquid (water), and gas(humidity). Their relative presence and internal phase transitions are the significant atmospheric transitional factor for the stability of life and chemicals. The presence of water molecules also describes the structure and formation of different metamorphic rocks and their segregation. Therefore, the precise labeling of humidity is important for the atmosphere, biological, and chemical transition. The presence of humidity is expressed in different ways.

Absolute humidity

This is the mass of water vapor present in a defined or fixed volume of gas and is expressed as mg/ml or g/m^3. It is the density of water vapor in the wet air and mathematically represented in Equation 1.

$$Absolute\ humidity = \frac{Mass\ of\ water\ vapor}{Volume\ of\ gas} \quad (1)$$

Relative humidity (RH)

It indicates the ability of air to absorb H_2O molecules and is related to other parameters like temperature, pressure, and composition. It is the ratio of the mass of water vapor present in a known volume of gas relative to the same amount of saturated gas with water vapor at identical temperature and pressure. The mathematical expression for RH is shown in Equation 2 and is also indicating the water-absorbing capacity.

$$RH = \frac{Water\ vapor\ pressure}{Saturated\ water\ vapor\ pressure} \quad (2)$$

RH is also expressed into the scale of hundred as indicated in Equation 3 and is called a percentage relative humidity(%RH).

$$\%RH = \frac{Water\ vapor\ pressure}{Saturated\ water\ vapor\ pressure} \times 100 \quad (3)$$

Moisture content

It is the amount of H_2O molecules present in 1 kg of dry samples i.e solid, liquid, and gas. It can compute by the ratio of no molecules and molecular mass of H_2O and samples. Currently, it is important in relating the purity of commercial and laboratory samples,

In general, the monitoring of humidity is a very ancient practice for the prediction of weather and rain condition. Initially, it was in practice by "Shang-Dynasty" of china during 1800 bc by comparing the change in mass of bar of charcoal kept in dry and humid conditions. In a particular humid condition, the extent of adsorption of the water molecule is related humidity of the atmosphere [**16**]. The other way to measure humidity is by monitoring temperature-dependent condensation i.e., Dew points (DP). Generally, DP is the temperature, at which water molecules present in the air condense into liquid-like during rain. As gas is cooled it reaches a temperature at which it can hold no more water vapor and is fully saturated. Any further cooling causes condensation of the water vapor into liquid form. The DP is the express the presence of H_2O molecule in air at different temperatures and is exploited for sensing humidity.

However, with time improvements in measuring techniques have also extended for sensing of humidity like monitoring of several secondary parameters like resistance, capacitance, impedance. oscillating frequency, refractive index. Currently, the interacting behavior of water molecules with humidity sensitive molecules develops secondary emission and magnetism has been explored for precise detection of humidity molecules. The nature of interaction governs the sensing mechanism and it was initially proposed by proton diffusion and mobility of hydroxide ions. The later humidity sensing mechanism was explained in terms of surface adsorption, which is either physical or chemical depends on the sensing materials as well as porosity and they are interlinking [**17**]. Thus, the adoptable principle for humidity sensing is based on monitoring adsorption based responsive change of humidity sensitive materials using a humidity-controlled chamber. The maintenance of specific humidity levels is another important step for generating the standard for the desired amount of humidity in a controlled isolated chamber. For this purpose two methods are in practice: a) mixing of moist air with 100 % humidity and absolute dry air with 0% humidity in a variable predetermined ratio, b) use of the different saturated salt solution in an airtight chamber attached with the mini fan. The list of saturated salt solutions suitable for maintaining humidity levels is listed in **Table 2** along with the temperature effect [**18**].

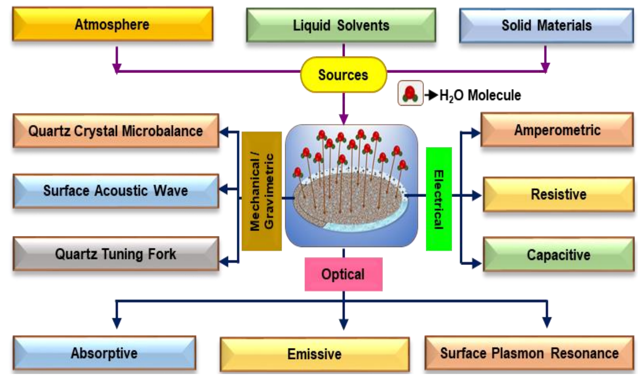

Fig. 2. Different types of humidity sensors.

Gravimetric and mechanical sensors

In gravimetric sensors, the change in mass or gravimetric forces induced properties are monitored against the different levels of water molecules present in the surrounding. One of the simple gravimetric sensors is "psychrometry", which is consists of two words i.e., "psuchron" means cold, and "metron" means measurement. In these techniques, some hygroscopic substances like cotton, paper, cellulose, other wood products, sugar, calcium oxide are allowed to attract the humidity present in the surrounding atmosphere. This surface interaction of water molecules changes the different thermodynamic parameters like temperature, which are monitored to calculate humidity present in the surrounding. This method is reported very promising for monitoring humidity after exploring the surface acoustic wave (SAW), quartz crystal microbalance (QCM), and sensors work on piezoelectric effect i.e., based on modulation of interactive surface accusative waves, frequency, and piezoelectricity. However, the cantilever sensors is a piezo restive sensor,

Table 2. List of saturated salt solution with temperature-dependent maintained humidity [18].

Temperature(^{0}C)	KCl	NaCl	NaBr	$MgCl_2$	CH_3COOK	KCO_3	$MgNO_3$	$SrCl_2$	LiCl
10	86.8	75.66	62.2	33.5	23.7	43.1	57.4	75.7	11.3
15	85.9	74.13	60.7	33.3	23.4	43.2	55.9	75.6	11.3
20	85.1	72.52	59.1	33.1	23.1	43.2	54.4	75.5	11.3
25	84.3	70.85	57.6	32.8	22.5	43.2	52.9	75.3	11.3
30	83.6	69.12	56.0	32.4	21.6	43.2	51.4	75.1	11.3
35	83.0		54.6	32.1			49.9	74.9	11.3
40	82.3		53.2	31.6			48.4	74.7	11.2
45	81.7		52.0	31.1			46.9	74.5	11.2
50	81.2		50.9	30.5			45.4	74.4	11.1
55	80.7		50.2	29.9				74.4	11.0
60	80.3		49.7	29.3				74.5	11.0
65	79.9		49.5	28.5				74.7	10.9
70	79.5		49.7	27.8				75.1	10.8
75	79.2		50.3	26.9				75.6	10.6
80	78.9		51.4	26.1				76.3	10.5

Further, the induced responsive changes of materials viz mass for gravimetric sensors, resistance, capacitance, impedance for electrical sensors, and optical permeability, and florescence for optical sensors are measure. These responsive properties are the basis for the classification of humidity sensors for different materials are shown in **Fig. 2**.

which is based on the monitoring of humidity induces sensor of humidity sensitive materials like polymer composites. In general, this type of humidity sensor offers high sensitivity, quick response time after employing the simple instrumental setup. However, these sensors require expensive driving and advanced detection components [**19**].

Electrical sensors

Most of the commercialized humidity sensors are electrical types and works on the monitoring of humidity-induced electrical properties i.e., resistance, capacitance, impedance developed after adsorption of water molecules. The simple principle of electrical types humidity sensing is based on proton conduction due to multilayer adsorption of H_2O molecules. The initial layer of water adsorption is non-ionic, but the successive adsorptions are ionic. This ionic adsorption of water molecules allows facile electrical conduction and its intensity has been used to identify the humidity in its surrounding. The mechanism for electrical type humidity sensing has been illustrated in **Fig. 3** along with the sensing setup.

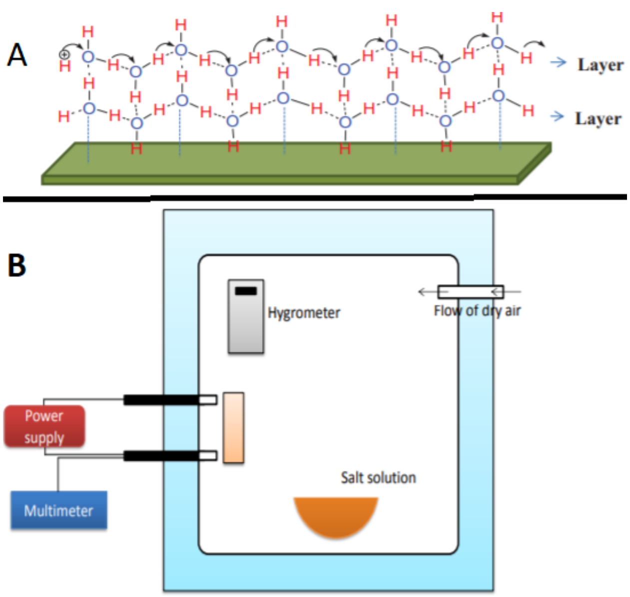

Fig. 3. Schematic and mechanism for electrical type humidity sensing [20-21].

The presence of ions on the surface also changes the electrical resistance as well as impedance and the sensor are referred to as resistive types humidity sensors. Similarly, the ionic adsorption also changes the capacitance of the sensing substrate and this class of sensor is referred to as capacitive humidity sensors. Currently, each type of electrical type sensor is reported with its own merits and demerits after employing a wide spectrum of materials and sensing devices. A simple proposed electrical resistive type humidity sensor is shown in **Fig. 3(b)**. The sensor used 200 nm thick zinc oxide doped polyaniline nanocomposite as humidity sensing materials of the closed atmosphere in the range 5 to 95 RH with sensing parameters i.e., response time, 32 sec; and recovery time, 45 sec. The humidity of the chamber was maintained using the different saturated salt solution and monitoring resistance by a simple laboratory multi-meter after making electrical contact with silver paste [**21**].

Optical sensors

This class of humidity sensors works on the monitoring of humidity-induced optical properties of materials like refractive indexes, surface plasma resonance (SPR), and fluorescence [**22**]. The advantageous features of this class of sensors are immunity to interference by electrical and magnetic force, miniaturization, and quick sensing properties. The basic principle is surface interaction of water to humidity sensing substrate generates changes in refractive index, quenched fluorescence, induces surface plasma resonance for quantified sensing of water molecules. Based on this principle several optical sensors are reported with certain modifications or improvements. In this regard, the use of optical fiber technology is reported as an efficient transmitting medium for humidity sensing response. Shukla *et.al.*, has used a u-shaped glass rod coated with nano-sized magnesium oxide coupled with optical fiber for efficient monitoring of humidity in a wider range after monitoring the light output in the range 5 to 95 % RH, the proposed optical sensing setup with all labeled integral components are shown in **Fig. 4**.

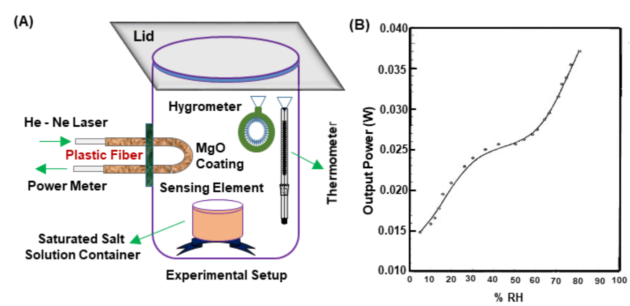

Fig. 4. Glass coated optical fiber and optical fiber coupled humidity sensors and sensing behavior [23].

The basic underlying principle is the change of numerical aperture after adsorption of humidity on MgO coated on optical fiber. The change in numerical aperture changes the optical output measured by the attached power meter. The change in the output depends on the hybrid refractive index of cladding and maybe increases or decreases. The trend in the variation of output power against different %RH is shown in **Fig. 4** after adsorption H_2O molecules of MgO surface.

SPR is another significant surface optical phenomenon that occurs on the metal-dielectric surface and highly sensitive to external molecular interactions, phenomenon, and change in the refractive index. Thus, surface polished and coated optical fiber has been highly sensitive to measure relative humidity present in the surrounding. The used coating materials have a significant role in humidity sensing from visible to the ultraviolet range and some of the compounds used in coating are graphene, tungsten sulfide, molybdenum sulfide. The coating of the hybrid layer like ultra-thin gold and graphene enhances the sensitivity of humidity significantly by 90% with optimized thickness and sensitivity of 5,601.1 nm/RIU [**24-25**]. The interacting quenching inflorescence due to water molecules with a chromosome is another tool to measure precise humidity sensing. In this regard, Gupta and Boom have designed a redox-active Osmium Chromophore-Based Monolayers for quenching of fluorescence in the presence of ppm level water molecule present in organic solvents i.e., tetra hydrofuran [**26**]. The reported change in absorbance is shown in Figure along with structure developed sensitive molecule in **Fig. 5**.

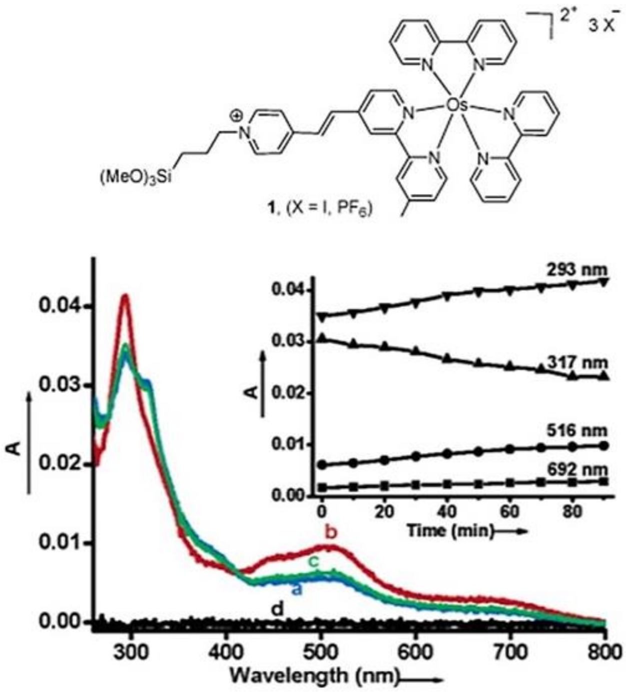

Fig. 5. Osmium Chromophore-Based Monolayers for ppm level humidity sensing [26].

The processing and design of sensors are other criteria for improving the efficiency of humidity sensors. In this context, both chemical (sol-gel, precipitation, grafting, emulsions) and physical methods (chemical vapor deposition, sputtering, laser deposition) are explored for making a humidity sensing layer as a thin layer, monolayer, pellet, and thick film. Although, the chemical method is cheaper and performed in limited resources with compromised purity. Further, the physical method gives better purity materials but the infrastructure required is very costly with precise monitoring. Therefore, still, intensives efforts are in the process of designing a better tool for preparing humidity-sensitive materials. For example, the reduction of temperature of reaction bath for preparation of humidity sensitive conducting polymer composite is reported after metal oxide functionalization of polymer monomer like polyaniline and polypyrrole [**27**]. 3D printing is another promising processing tool to develop better humidity sensing substrate after synergizing chemical processing and computer-aided design. This technique bears several advanced features like précised thickness and shape control to design better humidity sensitive substrates [**28**].

Sensing mechanism

The basic principle in humidity sensing is the monitoring of induced properties after adsorption of humidity of water. In ancient times the monitoring of change in weight after adsorption of moisture was in practice for humidity monitoring using different adsorbents like charcoal. However, with the advancements in monitoring techniques, several secondary parameters like conductance, resistance, capacitance, impedance, molecular frequency, refractive index, optical output, and luminous properties are monitored in precise humidity sensing. However, the basic properties of water molecules like high dielectric constant, heat capacity, ligand nature, and refractive index are key in the humidity sensing mechanism. For example, the chemisorption of water molecules on metal oxide does not allow conduction of electricity in the first adsorption layer but the subsequent layer of physical adsorption generates hydronium and hydroxide, which changes the resistance of sensing substrate is resistive type sensing. This proposed humidity sensing mechanism over structurally optimized cupric oxide and polyaniline nanocomposite is explained in **Fig. 6**.

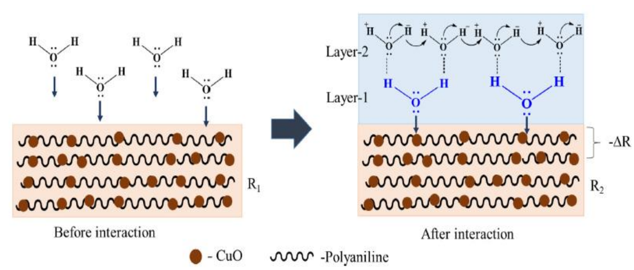

Fig. 6. Resistive type humidity sensing mechanism on CuO/PANI nanocomposite [27].

Similarly, the adsorption of water molecules over nano-sized zinc oxide coated optical fiber generates the hybrid refractive index due change in the relative refractive index of the cladding of the optical fiber. The formation of the hybrid layer changes the numerical aperture of optical fiber as per Equation 4.

$$Numerical\ aperture(NA) = sin\theta = \sqrt{n_c^2 - n_l^2} \quad (4)$$

Here, nc and nl are the refractive indexes of both interacting layers on optical fiber and θ is the angle of incidence of light on optical fiber. The change numerical aperture yields the variable permeability of light through the optical guide for the varied range of sensing of humidity i.e., 5-95 RH [**29**]. Further, the adsorption of H_2O molecules on a surface of a crystal changes the frequency, and this change in frequency quantitatively depends on the concertation of water molecules present in the surrounding crystal. The relation of frequency change related to the

Sauerbrey equation as indicated in Equation 5 is the basis for gravimetric sensing.

$$\Delta m = c.\Delta f \qquad (5)$$

Here m is the mass of the adsorbed molecule, c constant and f frequency of crystal respectively. The representative result of QCM based humidity is shown in **Fig. 7** due to the change in frequency of QCM coated with hydrophilic cellulose layer for humidity monitoring.

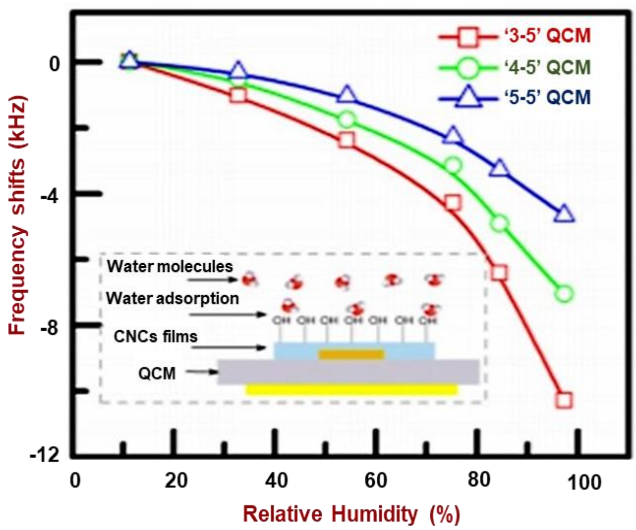

Fig. 7. Frequency response curves of CNCs based QCM humidity sensors as a function of humidity [30].

Humidity sensitive materials

The basic properties of the material explored for humidity sensing are hydrophilicity, porosity, doped ion mobility, interactivity, and ionizable water adsorption. Initially, the differential water adsorbing capacity of molecules was explored for humidity sensing due to the interesting adsorption capacity of materials. Later, the observed limitations are hydrolytic un-stability of sensing matrix was realized after adsorption of water. Thus, with time other strategies are adopted like activating sites, optimized porosity, and channeling the matrix for better sensing of humidity. Another, dimension in improving the humidity sensing in materials is size optimization, dimension control, and structural designing in materials science. These manipulation advances several advantageous features like small size i.e., nano dimension develops adsorption, dimensional control develops better channelizing communication of sensing and doping of interactions like magnesium in zinc oxide for better sensing, Further, the flexibility, spinnability, and print capacities are other advancements of humidity sensing materials for the development of effective sensors. Several materials advances are reported for making humidity sensors flexible, implantable, pintable, and spinnable for better applications of humidity sensing behavior [**31**]. Some current applications of humidity sensors are shown in **Table 3**.

Table 3. Representative applications of humidity sensors.

S.N.	Area	Specific applications
1	Weather station	Rain for casting by comparing the relative humidity
2	Medicals	Breath monitoring, optimum condition as humidity allows the growth of virus and bacteria
3	Packaging	Food safety, Labelling, shelf life, and leakage
4	Automotive	The air quality of engine for the better life of the engine
5	Refrigerator and air conditioners	High humidity increases load due to the high heat capacity of water molecules
6	Chemical laboratory	The purity of chemicals and solvents
7	Electronic devices	Life of battery, solar cell, and LED
8	Agricultural practices	Plants health and productivity

In the context of the above development different classes of explored humidity sensing materials are discussed in the following categories.

Ceramic

Ceramic is a high-temperature stable compound, hard, brittle, corrosion-resistant, dielectric, and non-metallic materials. It is mainly comprised of metal oxides, nitride, carbide, and perovskite-type amorphous and crystalline with aligned properties and interactive nature. It is widely used in medical, electronic, casting, and chemical sensing including humidity sensors. The use of ceramic in humidity sensing application is due to surface adsorption of water molecules on the ceramic surface due to unique structure i.e., consisting of grains, grain boundaries, and pores to promotes adsorption process [**32**]. The adsorption of H_2O molecule develops induced electrical, optical, and mechanical properties to develop different types of humidity sensors [**33**]. The adsorption took place in a heterogeneous manner i.e., physio-sorption and chemisorption due to the formation of surface hydroxyls, which depend on temperature and porosity. The presence of porous nature also permits capillary condensation of water molecules for the effectiveness of electrical types humidity sensing according to equation 3.

$$rk = \frac{2\gamma M}{\rho RT\ln(\frac{Ps}{P})} \qquad (3)$$

Here, the meaning of the symbols is rk (Kelvin radius), P (water-vapor pressure), Ps water-vapor pressure at saturation, γ (surface tension), p (density), and M is the molecular weight of water respectively. The water condensation takes place in all the pores with radii up to rk, at given temperatures and water-vapor pressures. The smaller the rk, or the lower the temperature, the more easily condensation occurs. The balance between adsorption and condensation decides effective sensing range and properties. Another aspect in ceramics to improve the adsorption is doping of other ionic metal ions like magnesium in aluminum oxide and iron oxide [**34**]. The size reduction and thickness is another dimension in optimizing the humidity sensing properties. For example, Wange *et.al.*, has reported that nanocomposite prepared from nano-sized TiO_2 and K0.5Na0.5) NbO_3 using a hydrothermal method exhibited better impedance-type humidity sensing properties by two to four times higher than the constitutes. The reported sensing range is 12 to 94% along with response and recovery time by 25 s and 35 s along with very small hysteresis [**35**]. The adsorption behavior also varies with the level of relative humidity i.e., lower RH allows physio sorption, while higher relative humidity allows chemisorption. The illustrative adsorption trends at different relative humidity are illustrated in Figure 8, while the mechanism follows defect progress mechanism to respond against humidity.

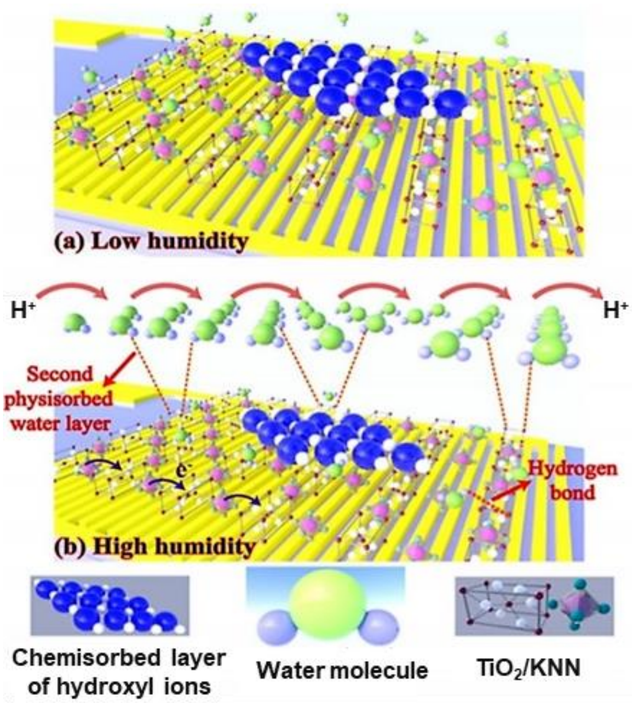

Fig. 8. Adsorption of TiO_2/(K,Na)NbO_3 Nanocomposite at different RH levels [35].

Another advance in ceramic-based humidity sensors is transparency with better sensing parameters. Wang et. La has reported a transparent humidity sensor from morphology controlled film of molybdenum oxide. The film was prepared by the single-step spin coating method using the green reaction bath. The observed sensing parameters are 85% transparency in the visible region along with a small response time of 0.97, recover time of 12.11 s and sensing range of 11 to 95% [**36**]. The oxide coated substrate also generates an optimized refractive index for the quantification of interacting water molecules. Shukla *et. al.*, have coated a glass rod with nano-sized zinc oxide (70-90 nm) and coupled with optical fiber using an identical set up shown in Fig. 4 for humidity sensing of a closed atmosphere with sensing parameters viz 30 s response 30, 35 s recovery time, 0.45 sensitivity in the humidity range of 5–50 and 0.30 in the humidity range of 50 to 90. The thickness, nature of sensitivity, interactions, and mechanism were also reported by monitoring relaxation time against relative humidity [**37,38**]. The ceramics are also explored for humidity sensors using quartz crystal microbalance techniques. Farzaneh et.al has reported a humidity sensor using quartz crystal using nanostructured copper doped titanium oxide by sol-gel technique. The reported experimental setup of the humidity sensor was depicted in **Fig. 9**.

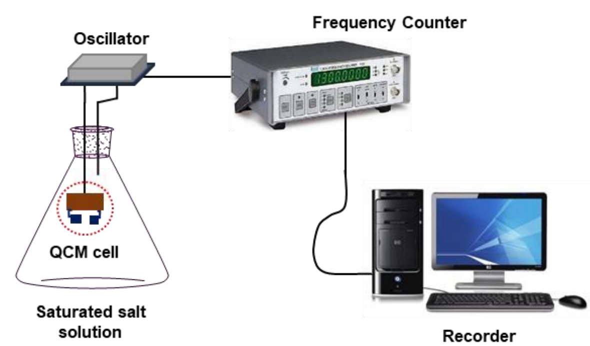

Fig. 9. Titania coated QCM based humidity sensor [39].

The sensor was reported suitable for humidity sensing in the range of 30 to 70 RH after obeying the modified Langmuir model. The doping of copper in TiO_2 reduces the band to make it more interactive and sensitive to interacting water molecules [**39**]. Some other important ceramic-based humidity sensors are summarised in **Table 4** along with monitoring properties, sensitive substrate, and sensing parameters.

Table 4. Ceramic based humidity sensors along with properties.

S.N.	Materials	Transducers	Properties	References
1	α-MoO_3	Impedance	Response time 0.97s, recovery time 12.11s, and sensing range 11 to 95 RH	40
2	$BaTiO_3$	Capacitive	Response time 40 s and recovery times 25s	41
3	Magnesium Oxide	Impedance and capacitance	Sensing range 11.3–67% RH, response 13s and recovery time 61 a	42
4	Copper oxide	Impedance	Size dependant multilayer adsorption	43
5	$MoSe_2$/$CuWO_4$	impedance	Ultrahigh sensitivity, low hysteresis, and excellent repeatability	44
6	MoS_2 heterojunction	Resistance	Sensing range 20 to 98 % RH and 0.615 MΩ/%RH sensitivity.	45
7	BaSrTiO3	Impedance	Sensing range 20-95% RH	46
8	Tin Oxide	QCM	High sensitivity in 11%–97% RH	47
9	Tungston sulfide	SPR	Sensing range 58% to 88% RH	48
10	PVA/ZnO nanowire	Resistance	Sensing of soil moisture with sensitivity of 4.6 KΩ/0.1% RH, response time 40 s and recovery time 60s	49
11	Anodised alumina	QCM	Reversible sensor in 5s in 5 to 94 % RH	50

Carbon Nanostructure (CNS)

This class of materials includes the nano-sized and low dimension carbon allotropes, which mainly include carbon black, carbon fiber, carbon nanotube, fullerene, and graphene. This class of materials has emerged as a very fertile source in emerging areas including humidity sensors due to the wide range of properties amorphous to crystalline, semiconducting to metals. Another point is the low cost and easy availability of carbon-based resources like biomasses are other fascinating dimensions for using these materials by easy processing and treatment. For example, the carbon nanoparticles like biochar prepared from pyrolysis of biomasses are also frequently utilizes in humidity sensing purposes in the place of costly carbon nanotube and graphene. Currently, these materials are reported as high priority due to exceptional electrical, optical, physical, thermal, mechanical, electronic properties. These properties have been also attracted scientists for the preparation of the different classes of humidity sensors with improved electrical, optical, and mechanical properties [**51**]. Although the carbon nanostructure is normally hydrophobic, non-interactive with water molecules under normal conditions due to its nonpolar nature. However, the functionalization of these CNS like carbon nanotube develops significant interactive sites for humidity sensing. In another dimension the defect-free carbon nanostructure bears sp2 hybridized sidewall, noncovalent van der Waals forces and π stacking dominate the intermolecular interactions for sensing applications. Thus, the chemically modified CNT after plasma treatment exhibits better interactions with water molecules to work as e a better sensing platform with better linearity and sensitivity. The humidity sensing mechanism and interaction between the water molecules and CNT has been depicted in **Fig. 10**.

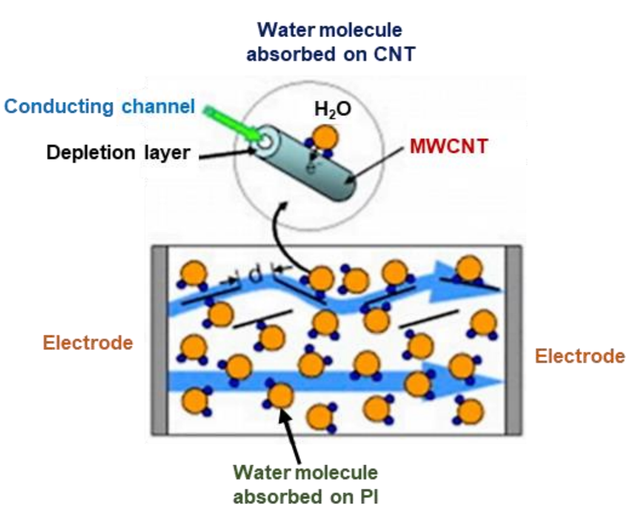

Fig. 10. Electrochemical humidity sensing mechanism over chemically modified CNTs [52].

Another important CNS used in humidity sensing is graphene. The basic difference between graphene and carbon nanotube is dimensional stabilization from 2D and 3D, which also changes the runnable band gap i.e., zero along with mechanical and electronic properties. The graphene and its composites have exhibited huge potential in humidity sensing as the field-effect transistor (FET), electrically and optically active sensing substrate and coating materials for SAW devices, QCM and OF based humidity sensing setup due to high specific surface area, electron mobility along with low electrical noises [**53**]. The humidity sensing on graphene electrode is also based on monitoring adsorption-induced properties like resistance, impedance, capacitance, etc. A simple illustrative principle and mechanism for humidity sensing are shown in **Fig. 11**.

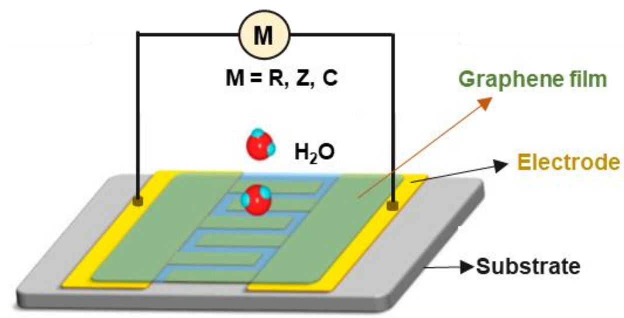

Fig. 11. Schematic for graphene-based electrochemical humidity sensors [53].

Another modification in graphene is oxidized graphene, reduced graphene, and graphene with quantum dots, which advances the several properties of graphene for humidity sensing. In example, graphene oxide contains oxygen along with graphene and the presence of oxygen makes the graphene surface more hydrophilic for a better adsorptive and interacting surface. Apart from oxygen, other elements like fluorine are also doped in graphene for developing better interacting surfaces for humidity sensing applications. This graphene and water molecule surface interaction has been also explored for optical fiber-based humidity sensors and gravimetric sensors [**54**]. For example, Zhang *et. al.*, have developed laser-scribed-graphene humidity sensors using a commercial DVD, the procedure for preparation is represented in **Fig. 12** [**55**].

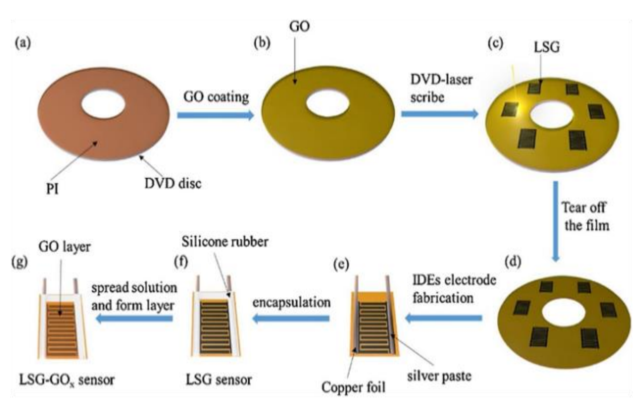

Fig. 12. Schematic fabrication of graphene-based DVD for humidity sensors [55].

The developed DVD sensor exhibits the RH sensing parameters i.e., sensitivity of 4770.14 pF/% RH and working stability is more than 30 days with the potential for production of tailored RH sensors. Some other important graphene-based humidity sensors are listed in **Table 5** along with sensing methods and parameters.

Table 5. Graphene-based humidity sensors with the method and sensing parameters.

S. N.	Composition	Transduces	Sensing parameters	Reference
1	Graphene Oxide	Optical fiber grating	Sensing response 2.53 pm/% RH in the sensing range of 20%-70%RH,	56
2	Tin disulfide/ reduced graphene	Self-powered voltammetry	wide RH range and human breath	57
3	Fluorinated Graphene	Resistive	Sensing range 20% to 80%, and sensitivity of 0.22%/% RH	58
4	Graphene oxides	QCM	Sensing range 5.60 % RH to 2.53 % RH	59
5	Single-walled carbon nanotube/ Graphene	Electrical types	5–80% with response/recovery time of 198/110 ms	60
6	Polyaniline-encased multiwall carbon nanotubes	Electron transfer resistive type	Flexible human respiration monitoring	61
7	Chitosan/zinc oxide/single-walled carbon nanotube	Chemiresis-tive	High sensitivity and good reproducibility.	62
8	Graphene oxide	Optical waveguide	Moisture sensing in transformer oil	63
9	Graphene/WS_2	SPR	Better limit of detection 6.8×10^{-4} %RH	64
10	Carbon Nano coil	Resistive type	Quick response and recovery time of 1.9 s and 1.5s respectively.	65
11	Carbon dot	Colorimetric sensor	Sense water in organic solvents	66
12	Biochar	Resistive	Reasonable sensing parameters	67

Polymers and their composites

The highly stable, processable, and functional features of polymers are the fascinating properties to explore in humidity sensing applications. Although the organic polymers are hydrophobic in nature, but the doping, plasma treatment, encapsulation of metal oxide, and oxidation in polymers generate selective hydrophilic interaction between a water molecule and polymeric surface. In the example, the sulfonation in polystyrene develops interactive behavior with partial ionization and suitable for sensing application. The sulfonation of commercial polystyrene by 22 % generates a change in properties for interaction with relative humidity between 3–90 RH%, which allows significant changes in its impedance for humidity sensing with a quick response time of less than 30s [**68**]. The interaction between water molecules and polymers yields different induced electrical, optical, and gravimetric response for efficient humidity sensing. The inclusion of metal oxide, metal, and carbon nanostructure generates high adsorption capacity, porosity, and stability in polymer-based sensing substrate. For example, the addition of nano-sized metal oxides like tin oxide in the matrix polyaniline matrix has developed effective interacting sites for humidity sensing with sensing effective sensing parameters. The illustration for the structure of tin oxide encapsulated polyaniline along with sensing behavior in comparison to pristine polyaniline is shown in **Fig. 13**. The study reveals that the addition of tin oxide nanoparticles improved the sensitivity of PANI by 8.8 times with better sensing properties [**69**].

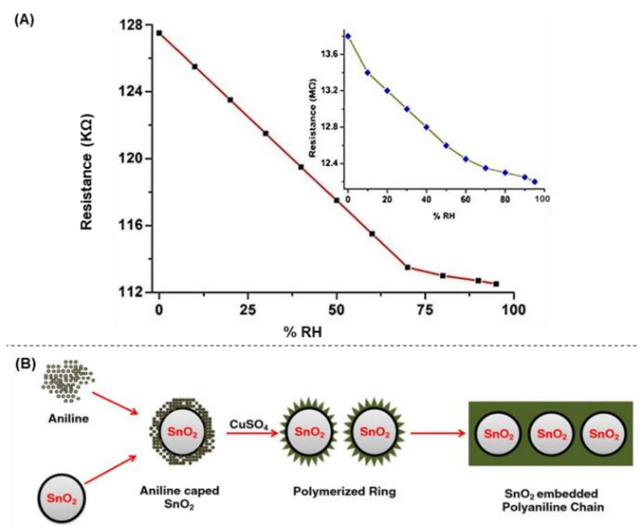

Fig. 13. Chemiresistive type humidity sensing over SnO2/PANI nanocomposite [69].

Similarly, the presence of ionic nanosize ZnO in the polypyrrole matrix generates an ionic matrix for effective single conduction. Thus, the developed partially ionized matrix has been found better interactive and conducting sensing substrate for humidity effectively. The reported sensing parameters like 12s response time, 8s recovery time with negligible interference in RH range of 5-95. The improvement in sensing properties is due to partial ionization in polymer along with hydrophilicity, further, the sensing mechanism has been depicted in **Fig. 14** along with brief results.

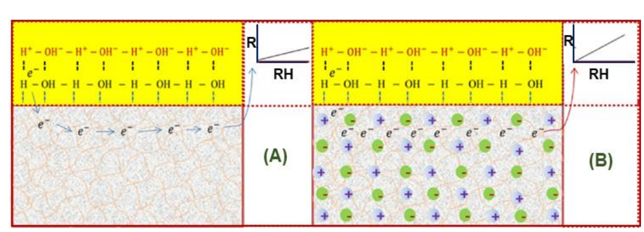

Fig. 14. Schematic for improvement in humidity sensing on ZnO/PPy [70].

Grafting of polymer is another tool to optimize the hydrophilicity and hydrophobicity, the optimization of these properties is another aspect to improve the sensing range of sensing substrate. In this regard, Shukla et .al has grafted cellulose with PANI and PPy using in-situ polymerization at moderate conditions. Thus, the obtained grafted matrix has been found suitable for humidity sensing in an extended range than pristine conducting polymers like PANI and PPy [**71,72**]. The responsive and ionized cellulose developed after treating with potassium hydroxide has been explored for resistive types humidity sensor as the transparent sensor with sensing good parameters i.e., 11.3−97.3% RH range, response time 6s and recovery time 10.8 s. These materials also offer the potential in real-time monitoring of RH of human skin as a modular moisture sensor component of an integrated intelligent wearable medical diagnostic devices [**73**]. Apart, from electrical sensing, the polymer is also widely used for optical and gravimetric humidity sensing purposes. In optical sensing, the presence of oxidized form, functional group, and unsaturation sites plays an important role in results induced fluorescence and optimized light permeability. Thus, developed chromophore has optical interactive nature for ppm level water present in organic solvents.

Optical sensing is based on monitoring of humidity dependent optical response in term of optical permeability, induced frequency, quenching effect with a quick response time and reliability [**24,6**]. The hydrophilicity and processable polymers are improved the layering behavior of quartz crystal balance and will add advances in QCM based humidity sensors. The polyethyleneimine-grafted polyacrylonitrile hydrophilic nanofibers have been used in QCM based humidity sensors exhibits better sensing parameters like sensitivity, selectivity, stability, and reproducibility. The better sensing properties are due to porous structures, high surface area, with efficient reversible adsorption/desorption process of H_2O molecules because of hydrogen bonding between the water molecules and the hydrophilic PEI groups [**74**]. Some other important polymer-based humidity sensors are documented in **Table 6** along with sensing materials and parameters.

Performance, prospects, and challenges

The proposed strategies in advancing the humidity sensing materials are optimized in terms of hydrophilicity, porosity, ionization, surface area, interactivity, processability, strength, and mechanical flexibility by suitable doping, grafting, and composite formations. The addition nanogenerator by adding the moisture-sensitive electronically active oxides like titanium oxide to enable a humidity sensor work in the absence of external source energy as well as ensure the remotes workability for monitoring of humidity and remote sensing [**90**]. Similarly, the concept of self-activation has been added in humidity sensing the substrate for improving the efficiency and sensitivity of humidity sensors after adopting molecular level chemical engineering [**91**]. This concept also explores the possibilities to generate moisture dependent voltage generation for extended application of humidity sensing as an alternate source of energy with huge potential as a hydrolytic cell [**92**]. Another, objective in designing a better humidity sensor by controlling the thickness, dimension

Table 6. Polymer-based humidity sensors along with technical parameters.

S.N.	Composition	Transducers	Parameters	References
1	$ZnCo_2O_4$/PPy	QCM	Sensitivity 58.4 Hz/%RH, response 8s, and recovery times 7 s.	75
2	PPy and Ta_2O_5 Core-shell	Electrical type	response and recovery times of 6 s and 7 s	76
3	Cellulose nanocrystals	QCM	Improved sensitivity	77
4	PPy/SnS_2	QCM sensor	Enhanced humidity sensing	78
5	Poly(o-phenylenediamine-co-aniline	Resistive	Sensing ranging 11 to 97%, response time 38 s, and recovery time of 11 s	79
6	Cellulose Nanofiber/Carbon Nanotube	Amperometry	Excellent responsive property toward human breath	80
7	Calcium alginate hydrogel	Optical fiber	Excellent stability, repeatability, and time response	81
8	Polyvinyl alcohol	Refractive sensor	Sensitivity ~650 pm/% RH, linearity~ ~0.99 and sensing range from 35 % RH to 70 % RH	82
9	Carboxymethyl Cellulose/PANI	Impedance	Improved sensing parameter in range 25 to 75 RH	83
10	NiO/PANI	Resistive	Improved sensitivity	84
11	Chitosan	Fabry–Pérot interferometer	Breath monitoring	85
12	Doped acrylonitrile butadiene styrene	Resistive	Excellent sensitivity ~ 125-fold change in resistance in the range of 11–97% relative humidity	86
13	ZnO/PANI	Resistive	Wider sensing range	87
14	PANI/ Niobium pentoxide	Electrical type	Humidity sensing range 25% - 95	88
15	Nano-Fibrillated Cellulose	Substrate Integrated Waveguide	Low-cost sustainable and renewable material.	89

control of humidity sensing materials as a humidity sensing substrate engineering. The designing of sensing substrate has also a significant impact on humidity sensing, for example, the U-shaped glass rod is more effective for humidity sensing using optical fiber techniques than straight rod shape. It explores the importance of designing of sensing substrate for efficient humidity sensing [**25**]. Further, the importance of processing technique also significantly improves the humidity sensitivity like aerosol deposition of perovskite-based nanocomposite has been improved drastically sensitivity i.e., 21426 pF RH%$^{-1}$, with superior linearity 0.991 and excellent stability than perovskite-based humidity sensors [**87**]. In the current time, flexibility and printability are other issues in developing better humidity sensing. For example, the flexible humidity substrate can be easily attached with a substrate to develop effective humidity sensing devices [**88**].

Although, the importance humidity sensing is in the prediction of atmospheric events are well established but currently, the humidity sensor has other newer dimension of application like monitoring of human condition by respiration or breath monitoring, agricultural, electronic device and industrial plants [**93**]. Humidity monitoring in inhales and exhale air is a simple method to monitor respiratory conditions of humans, individual stress, cardiac and arterial vascular dysfunction. An innovative fabric has reported from graphene oxide with potential to effective monitoring of respiration rate and heath conditions with appreciable sensing parameters as shown in **Fig. 15**.

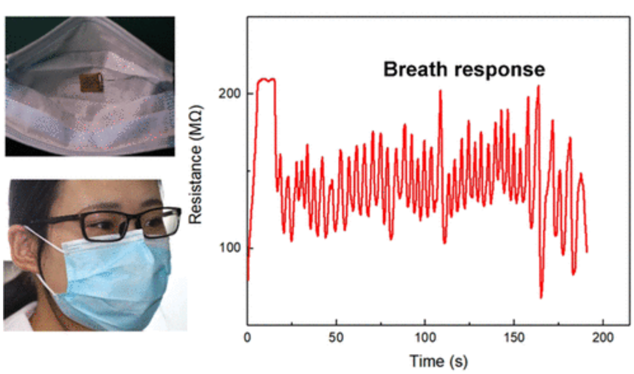

Fig. 15. The fabric for humidity sensing based respiration monitoring [**94**].

The presence of high humidity in exhaled gas contains other organic compounds like acetone, toluene, and serves as a biomarker for disease and metabolic conditions as well as moisture contents in body organs like skin [**95**]. This interrelated aspect and effect of humidity exercise the monitoring of humidity along with temperature for critical multiple sensing of human health and analytes. The degradation of biological organs changes the extent of RH in soils, thus the sensing of the precise level of humidity is not only essential to the agricultural chemist but also solves the cases of crimes as supporting documents for decay dead body including humans. The monitoring of humidity level also helps to screen the physiological process in plants like flowering, plant health, the moisture level in plants body, and transpiration. The potential of the humidity sensor is appearing like a multimodal flexible tool for monitoring integrated problem agriculture and plants health managements to productivity [**96**].

The thermophysical properties of H_2O molecules have explored its application as the coolant in several industries including the power plants in a close loop for judicious and conservative consumption of water. However, the leakage and its loss of coolant from steam generated have been reported for several failures and accidents. In this regard, Kim et. al has developed an optical fiber-based humidity sensor for testing the leakage of coolant i.e., water molecules from a power plant with the potential of its wide applications efficient point leakage monitoring [**97**]. Similarly, the presence of humidity changes the electrical properties of the electrode used in electronic devices like batteries and solar cells. Thus, the monitoring of humidity in working of these devices is important in extending the use of humidity sensor with prolonging workability [**98**] Thus, effective monitoring of precise humidity level has potential for real-time working a stability monitoring of electronic devices like the solar cell in term of generation current and potential under different humidity levels [**99**].

Although, several reports are available as a proposed commercial product in the form of a wearable band or mask for individual applications for invasive health management technology developments are still required [**100**]. Another concept for the incorporation of self-activation and powering has been a promising concept for the use of humidity of sensor remote and consistent manner present in the soil, sweets, tea, and other edible items. These, integrated concept external enables the use of humidity sensing without the availability of external energy sources in real-time working monitoring of electronic devices, packed products, condition of power plants. It also promises to monitor humidity from the remote areas for monitoring as well as atmospheric prediction after including wireless connections [**101**]. The integration of design for monitoring of multiple parameters like humidity and temperature also required to be developed without external energy in line concept of outer door electronics for multiple point monitoring. The humidity integrated temperature and strain sensors need to be explored as monitoring wearable setup for drought and local microclimate for effective growth of plants, vegetations, and animals [**102,103**].

Conclusions

In summary, the importance of humidity sensing, mechanism, materials is reviewed in this manuscript along with its applications in diverse areas like atmospheric prediction, human health, agriculture, forensic and electronic devices. Although humidity monitoring is a very old technique its emerging newer applications always provoked scientists to advance the existing materials for effective sensing in gaseous and liquid both medium along with the possibility of real-time monitoring using wireless technologies. The humidity sensing materials are described in ceramic, carbon nanostructure, polymer, and composites along with exhibited sensing parameters like sensitivity, response, and recovery time. Finally, the success and existing challenges in optimum humidity sensors are reported along with their prospect in future applications.

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Keywords

Humidity sensing materials, sensing methods, sensing mechanism, applications, and challenges.

List of abbreviations

Carbon nanostructure	CNS
Carbon nanotube	CNT
Dew points	DP
Digital Versatile Disc	DVD
Field-effect transistor	FET
Optical Fibre	OF
Polyaniline	PANI
Polypyrrole	PPy
Polythiophene	PTh
Parts per million	ppm
Percentage relative humidity	%RH
Quartz crystal microbalance	QCM
Relative humidity	RH
Surface plasma resonance	SPR
Surface accusative waves	SAW
Water molecule	H_2O

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