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Rakesh Kumar Sonker
Kedar Singh
Rajendra Sonkawade *Editors*

Advanced Functional Materials for Optical and Hazardous Sensing

Synthesis and Applications

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The purpose of the series Progress in Optical Science and Photonics is to provide a forum to disseminate the latest research findings in various areas of Optics and its applications. The intended audience are physicists, electrical and electronic engineers, applied mathematicians, biomedical engineers, and advanced graduate students.

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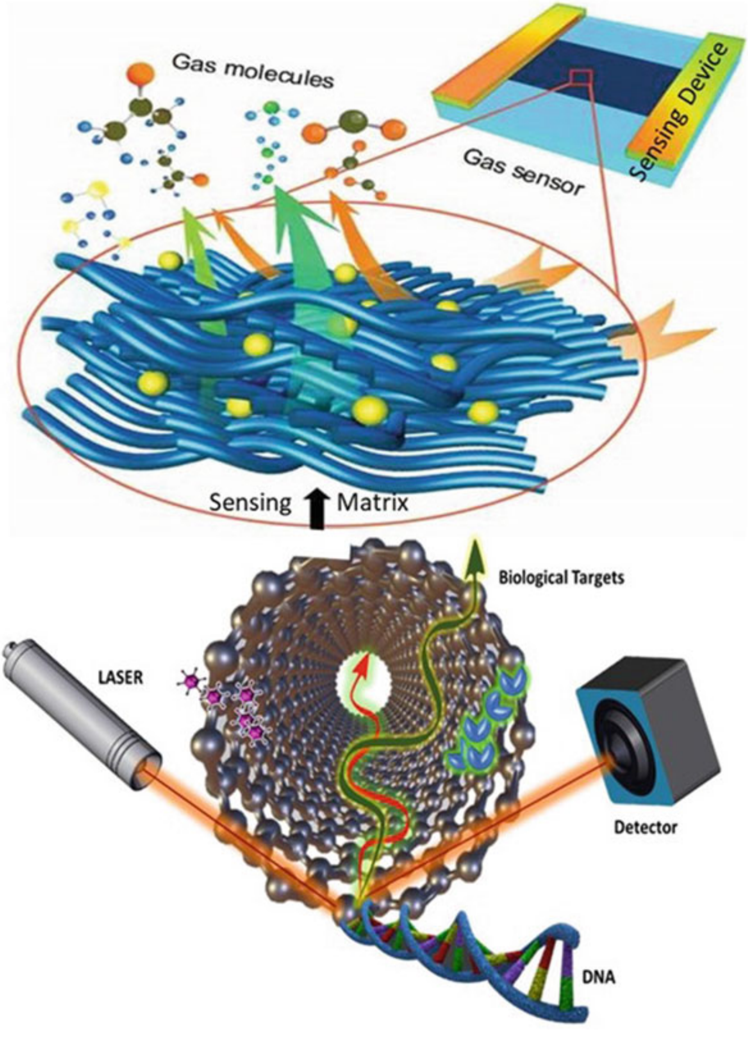
Gas molecules
Gas sensor
Sensing Device
Sensing
Matrix
Biological Targets
LASER
Detector
DNA

Preface

Over the past two decades, a great deal of research efforts have been made toward the development of optical sensing and gas sensing devices for practical applications ranging from toxic/inflammable gas detection to continuous environmental monitoring. Globalization is responsible for the emission of several toxic and hazardous gases. It is important to detect these toxic gases in the atmosphere and take safety precautions against them. Gas sensors play a pivotal role in domestic and industrial applications and also help to keep a cleaner environment by giving an early warning of leakage of toxic gases. A sensor is a device that provides a crucial way to detect the concentration and environmental information of gas that are found in chemical and petrochemical industries, agriculture, oil refineries, as well as food and beverage processing. Gas sensors cover a wide range of applications, and several materials exist in nature that can detect a variety of gases.

This book examines fundamental materials suitable for sensor design, general methods for the fabrication of sensing devices, the environmental impact of sensing devices, and micro-and nano-fiber-based sensing devices. It presents a detailed analysis of conventional optical and gas-sensing materials such as carbon-based materials, metal oxides, and metallopolymer nanomaterials. New trends in gas sensing materials include analysis of low dimensional, chalcogenides, Carbon nanotube (CNT), metal-organic framework (MOFs), and hybrid nanomaterials. Material scientists will find this book interesting, notably those engaged in the field of gas sensing materials research or those who intend to start researching in this area. This book comprehensively addresses the challenges and opportunities in the area of Optical and Hazardous Sensing. The contents of this book clearly address recent advancements in this area with relevant illustrations/figures. Chapters discuss the technology and difficulties facing both contemporary and future sensors, as well as fundamental features of concepts. This book is beneficial for researchers, students, academicians, and professionals working in the area of sensors. The book also discusses a few of the most popular characterization techniques for describing advanced functional materials. There are, in total, 12 chapters. Chapter An Introduction: Advanced Functional Materials for Sensing Application deals with the introduction of Functional materials and nanotechnology, which are the subject of advanced materials that have been designed and produced with the appropriate surface shape and properties for a particular function. Chapter Low-Dimensional Advanced Functional Materials as Hazardous Gas Sensing deals with the calculation of large surface-area-to-volume ratio, and advance materials; its structural, chemical, physical, and electrical properties of low dimensional advanced functional nanomaterials have been proven to be promising ultra-sensitive gas detectors. A good understanding of the Low-dimensional materials (0D, 1D, and 2D) have an extraordinarily enhanced surface-area-to-volume ratio, revealing a great number of interaction points with molecular analytes. Chapter Advanced of Chalcogenides Based as Hazardous Gas Sensing focuses on the effect of particle size on thermal, mechanical, electrical, magnetic, optical, and chemical sensitivity of chalcogenides. The chalcogenides nanostructure-based gas sensors have gained great attention in recent modern sciences as well as alternatives to the most promising materials emerging with a variety of potential applications and chapter covers the gas sensors based on nanostructured chalcogenides its attributes and development as gas sensor. Chapter Functional Materials for Biomedical and Environmental Sensing Application is devoted to the development of unique multifunctional targeted devices and functionalized materials for sensing, as well as cutting-edge monitoring sensors for anticipating molecular changes, which has advanced the efficiency of operations while lowering costs. This chapter discusses the synthesis of different functional materials for their practical applications in the biomedical field as biosensors and sensing of environmental pollutants. Chapter Carbon Based Functional Materials as Hazardous Gas Sensing deals with recent developments in electrical gas sensors for hazardous gases employing carbon nanomaterials (CNMs) and their hybrid/composite materials. Chapter Carbon-Based Functional Materials for Optical Sensors focuses on optical sensors and its wide range of carbon-based functional materials, which have revolutionized the field of sensor technology for the development of ever more sensitive devices. Chapter Metallopolymer-Based Sensor for Hazardous Gases, discusses the current accomplishments along with the upcoming challenges for metallopolymers functional material and their advanced gas sensing applications for environment monitoring. The thermal, mechanical, and electrical properties of metallopolymers and their applications are also discussed. Chapter Optical Sensors Based on Metal–Organic Frameworks focuses on surface-enhanced Raman spectroscopy (SERS) and luminescence, metal-organic framework (MOF) optical fibers that have received a lot of attention. This chapter provides an overview of the evaluation of recent studies of optical fiber sensors as well as the advancements in MOF-based optical detecting of ML and AI technology. Chapter Metrological Traceability of Optical Sensor deals with the metrological evaluation of optical fiber grating and optical biosensors is presented to provide a reasonable analysis of their performance. This chapter examines the difficulties of rapid on-site decision-making and real-time monitoring, and it analyzes potential methods to increase the effectiveness of the optical sensing method. Chapter Optical Sensors Based on Polymeric Materials deals with the synthesis, properties, and applications of conductive polymers (CPs). The applications for polymer-based sensors, such as all-flexible sensors, highly sensitive sensors, solid-state sensors, highly selective sensors, and stretchable sensors, are explained in detail. Chapter Utilization of Metallopolymer Nanomaterials in Optoelectronic Sensing presents a summary of recent advancements in metallopolymer NM-based sensors and their performance in detecting various analytes such as gases, biomolecules, and heavy metals. Chapter Nanomaterials for Food-Agritech Sensing Application focuses on the most recent advancements in scientific research on smart nanoformulations and delivery systems that enhance plant nutrition and crop protection, nanomaterials as smart food packaging material, and nanosensors for plant health and quality of food and safety monitoring.

We hope the readers will find this book inspiring and will be motivated to go deeper into the fascinating field of Advanced Functional Materials for Optical and Hazardous Sensing.

New Delhi, India — Rakesh Kumar Sonker
New Delhi, India — Kedar Singh
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An Introduction: Advanced Functional Materials for Sensing Application

Satyashila D. Ghongade, Pradnya G. Raje, Maqsood R. Waikar, Rakesh K. Sonker, and Rajendra G. Sonkawade

Abstract Functional materials are a subset of advanced materials that have been designed and produced with the appropriate surface shape and properties for a particular function. Researchers work to create sensors using materials that function at low temperatures and concentrations. These materials have great environmental stability and endurance, which provides various advantages over particular components and is commonly employed in sensor applications. This work emphasizes an overview of all types of classifications of sensors, the need for functional materials for sensor applications, progress in the research on sensors based on functional materials, and their sensing mechanisms. Finally, we comment on difficulties in the production of useful materials, user-friendly techniques for the fabrication of functional materials for sensing applications, and future research directions for further development in this field.

Keywords Functional materials · Hazardous gas sensor · Optical sensor

1 Introduction

In the twenty-first century, there has been a rapid advance in scientific technology and the social economy, which have utilized a significant influence on the environment. Because the environment is constantly exposed to harmful toxins and chemicals from a variety of sources, environment-sensing technology has piqued the public's

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interest [1]. As a result of industrialization and globalization, dangerous and toxic gases, including NO_2, CO_2, NH_3, H_2S, LPG, etc., are released into the atmosphere, endangering both human health and the environment. Hence, real-time monitoring of emissions of hazardous and toxic gases has emerged as a top priority. The need for hazardous gas sensors and their sources are illustrated in Fig. 1 [2]. The ideal mix of science and technology, and one of the best outcomes of these combinations, is the development of sensing devices. Sensing devices are intended to detect environmental changes and collect relevant signals [3]. Sensors are merely devices that monitor environmental inputs such as chemical, biological, and physical activity and transform them into readable qualitative and quantitative data [4]. A sensor is a device that converts physical phenomena into a measurable digital signal that can then be displayed, read, or processed further.

Sensors are designed and fabricated using a variety of materials. A few factors, such as a low detection limit, operationality at room temperature, high selectivity, excellent response and recovery time, low power consumption, pressure, stability in difficult environmental conditions, etc., determine which material is best to use. Metal oxides (MOs) [5], carbon materials [6], polymers [7], MXenes [8], metal–organic frameworks (MOFs) [9], quantum dots (QDs) [10], and other two-dimensional (2D) materials have all been used to develop a variety of gas sensors to suit these needs [11].

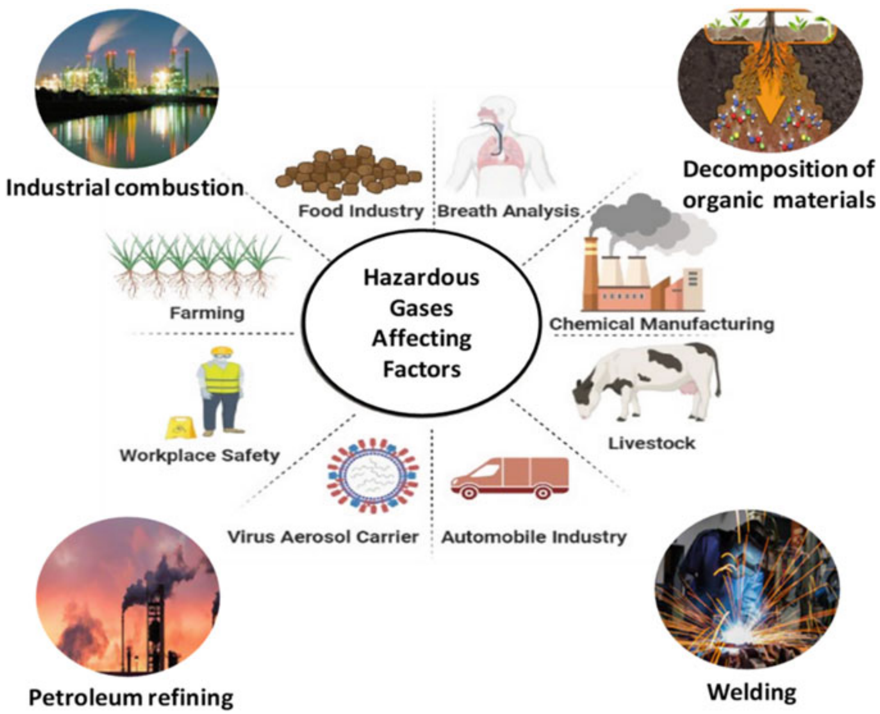

Fig. 1 Illustration of need for hazardous gas sensors and their sources

Working temperature has a significant impact on sensing performance, as was already mentioned. Thermal energy activation causes surface electron carriers to develop at higher temperatures, where they can react with airborne oxygen molecules to create a variety of oxygen species. Fewer electrons are generated at lower temperatures on the material's surface, yet such materials are thermally stable [12]. Making sensors from functional materials is an effective way to address these issues and improve response at lower working temperatures.

The chemoresistance concept, which refers to a change in material resistance, underpins the operation of metal-oxide-based gas sensors [13], which refers to a change in material resistance. This concept investigates the difference in electrical conductivity or resistivity of a material in contact with gas as its concentration changes [14]. The resistance value of the metal oxides is reduced or increased by oxidizing or reducing gas molecules or ions that interact with them. When a gas molecule interacts with the metal oxide surface, atmospheric oxygen residing on the metal oxide surface is reduced, allowing more electrons to enter the conduction band of the metal oxide material. This alters the thin film's resistivity or electrical conductivity. The majority of carriers in a metal oxide semiconducting thin film as well as the nature of the gas molecules at ambient temperature, i.e., whether they are oxidized or reduced, determine the resistivity of the film [15].

The inclusion of p-type and n-type material was found to boost the sensing response; this may be because of p–n junction formation [16]. Figure 2 shows the mechanism by which the p–n (ZnO/PANI) heterojunction forms. During the p–n junction formation, minority charge carriers in PANI require less energy to get the conduction band, but because ZnO is n-type and abundant in the sample, the n-type nature of films will dominate. For oxidizing gases like NO_2, only PANI will accelerate the rate of reaction [17]. The first oxygen species were adsorbed on the surface of air particles and then ionized into O_{ads}^-, resulting in the formation of a thin space charge layer and increased surface bending [17]. The electrons are transferred to the PANI due to its lower band gap than that of ZnO. As a result, an accumulation layer is formed at the ZnO-PANI interface. Before being exposed to NO_2, the film was stabilized and adsorbed by the p–n heterojunctions. The electron served as an electron acceptor in the process, and an acceptor surface state was seen. The Fermi level is brought close to the surface state because the surface state energy level is near the valence band edge. Fewer electrons are consequently transported from ZnO to PANI, increasing resistance. NO_2 releases trapped electrons into heterojunctions between ZnO and PANI after the supply of NO_2 is cut off, resulting in a decrease in resistance. As a result, this sensor structure can be used with confidence to detect NO_2 gas at commercial levels operating at room temperature [17].

The study of functional materials spans the entire spectrum of materials science, including physics, chemistry, biology, engineering, and nanotechnology. This field of study is very active and advancing today. Functional nonmaterials such as zero-dimensional (0D) nanomaterials, graphene, graphene-based materials, MOFs, QDs, and carbon nanomaterials have been investigated for use in sensing applications [18]. Mechanical and electrochemical sensing devices, optical sensing devices, biosensor devices, and semiconductor sensing devices that target air, water, bacteria, and so on

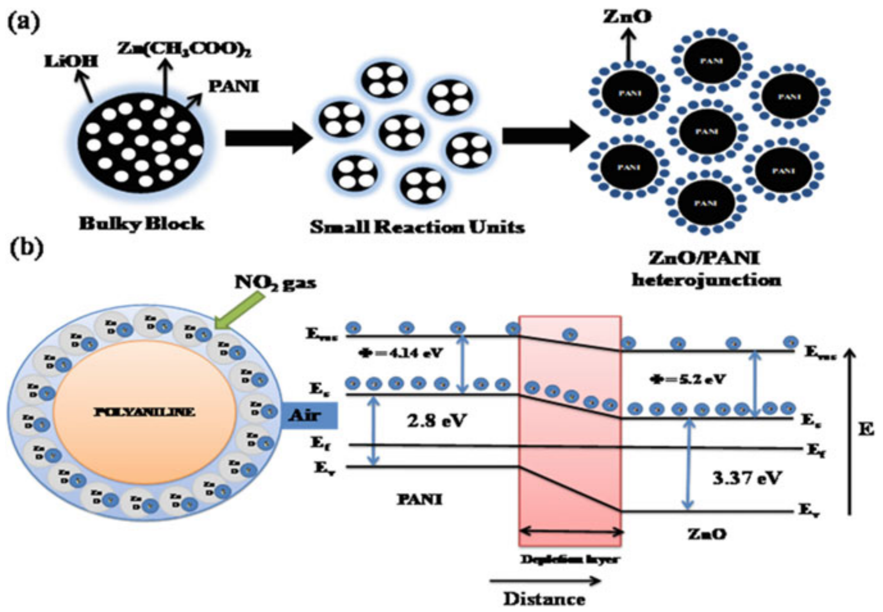

Fig. 2 Mechanism for the formation of ZnO/PANI (p–n) heterojunction

are examples of sensing devices [4]. We focused on advanced functional materials for sensing applications and briefly discussed hazardous gas sensors and optical sensors.

1.1 Need of Functional Materials for Sensor Application

Functional materials are a type of advanced, engineered material that has been created with a specific purpose through the use of appropriate surface morphology and tailored properties. Excellent properties of functional materials include a large specific surface area, mechanical properties, electrical properties, and optical properties [19]. As a result, functional materials are widely used in a variety of applications, including supercapacitors, catalysis, optics, smart coatings, biomedical, and sensing [6]. Functional materials used in a wide range of applications include semiconductors, dielectrics, superconductors, and magnetic composites [18]. The charge transfer procedure, catalytic interaction with an analyte, heterojunction generation, and their combination all improve the functional materials' sensing ability [20]. The complementary outcomes of the constituent materials produce the distinct properties of fabricated functional materials, which have a direct impact on the sensing mechanism and performance. Furthermore, the combination of two or more nanostructured materials produces multifunctional hybrid structures, which improve sensing performance. The functionalization state promotes a synergistic effect between the components

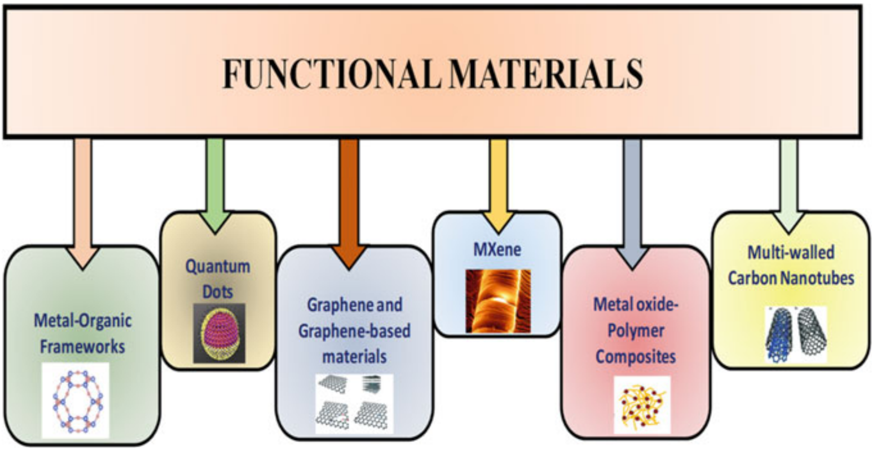

Fig. 3 General overview of functional nanomaterials for the fabrication of sensing devices

and has a significant impact on sensing applications by improving sensing parameters (i.e., sensitivity, characteristic response, selectivity, rapid response, and recovery time) [21]. For their improved sensing responsiveness, a large variety of functional materials, including MOFs, QDs, graphene and graphene-based materials, MXene, MWCNTs, and metal oxide-polymer composites, are widely available. A comprehensive overview of functional nanomaterials for the creation of sensing devices is shown in Fig. 3.

1.2 Advantages, Drawbacks, and Future Trends of Functional Materials for Sensing Application

Functional materials are becoming an increasingly important part of our daily lives for sensing, energy conversion, actuation, communication, and so on. These materials make use of their distinct physical, chemical, and structural features, and they frequently include intricate interactions of structural, magnetic, and electronic transitions with magnetic fields, electric fields, and thermal fields [22]. Functional materials offer several advantages for sensor applications, including [23]:

Selectivity: Selectivity can be achieved through chemical modifications or the incorporation of specific functional groups or receptors into the material.

High Sensitivity: Functional materials are often highly sensitive to changes in their surroundings, making them ideal for use in sensors. They can detect minute changes in temperature, humidity, pressure, or chemical composition, providing accurate and reliable data.

Stability: Functional materials can offer excellent stability, durability, and long-term performance, all of which are critical for sensor applications.

Versatility: Functional materials can be designed for a variety of uses, from environmental monitoring to biomedical sensing. They are adaptable to a variety of sensor platforms, including optical, mechanical, and electrical sensors.

However, there are also some drawbacks associated with their use [23]:

Limiting Operating Conditions: Some functional materials can only operate within a specific range of conditions, such as temperature or pH.

Stability Issues: Some functional materials can be unstable and degrade over time, resulting in sensitivity or selectivity loss.

Compatibility Issues: Functional materials may be incompatible with other materials in the sensor device, resulting in reliability and stability difficulties.

Functional materials are materials that have specific functions or features that make them appropriate for a given application or technology. Future trends in functional materials include 2D materials (graphene, boron nitride, and molybdenum disulfide) for use in electronics, energy storage, and sensing; smart materials, which have the potential to revolutionize fields such as medicine and engineering; and biodegradable materials, which can be broken down by biological processes such as enzymes and bacteria and have potential applications in packaging, agriculture, and medicine. Overall, functional materials have the potential to revolutionize many fields of technology and research, and their continued development will almost certainly lead to exciting new applications and discoveries in the future [23].

2 Classification of Sensor

A sensor is a device that detects and transmits an impulse in response to a physical stimulus (such as heat, light, sound, pressure, or a specific motion) (such as for measurement or operating a control). Further transmission of the information describing these changes is made to a variety of different electronics, most of which include a computer processor. An electronic device is always used in conjunction with a sensor. Sensors are classified in a variety of ways by specialists and researchers. The sensors are divided into active and passive categories in the first classification. Active sensors require an external excitation signal or a power signal. Passive sensors do not require any external power to operate and produce an output response. Active sensors, such as GPA and RADAR, must be powered by an external source [3]. Passive sensors, also known as self-generated sensors, produce their own electric signal and do not require external power. Examples include electric field sensors, thermal sensors, and metal detection [24]. In our daily lives, we use various types of sensors that are more accurate and allow for faster analysis. There are several types of sensors, such as temperature, proximity, infrared (IR), gas and smoke, alcohol, touch, color, humidity, and chemical sensors, which are shown in Table 1. We briefly

Table 1 Classification of sensor

Types of sensors	Uses of sensors
Temperature	To measures the changes in temperature.
Proximity	To detect the presence of an object.
Infrared (IR)	Used as proximity sensors in mobile phones.
Gas and smoke	To detect different gas such as LPG, Butane, Propane, Methane etc. and detect smoke due to fire.
Alcohol	To detects alcohol.
Touch	To recognize a finger or stylus touch.
Color	To detect any color in the field of color identification, image processing, industrial object tracking etc.
Humidity	For calculating relative humidity (a ratio of water content in air to maximum potential of air to hold water).
Chemical	To detect the pH value or the activity of specific ions in the solution, such as K, Na, and Ca.
Optical	To detect the physical amount of light rays and converts it into electrical signal.

discussed all these types of sensors, but we focused heavily on the hazardous gas sensor and optical sensor.

3 Techniques for Fabrication of Functional Materials

There are several approaches (both physical and chemical) for the fabrication of functional materials. The schematic classification of physical and chemical processes for the manufacture of functional materials is shown in Fig. 4. Some of these are listed below in brief.

3.1 Hydrothermal Method

The hydrothermal route is an effective method for producing functional materials with specific shapes, sizes, and compositions. The term "hydrothermal technique" describes those chemical processes that occur in an aqueous solution at high pressures and temperatures [25]. This method can achieve high temperatures and high pressures for a short period, ranging from several minutes to several hours in a closed reaction system. Hydrothermal growth of different nanostructures depends on various parameters such as temperature, precursors, the addition of surfactants, and the pH value of the solution. Under the hydrothermal condition, the density,

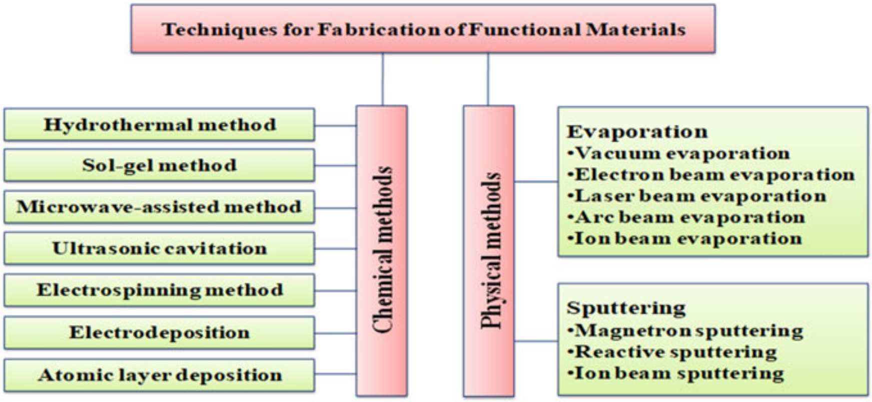

Fig. 4 Schematic of classification of physical and chemical processes for the fabrication of functional materials

pressure, and viscosity of the solvent changed, and various novel and unique shapes could be obtained using this method [26].

3.2 Sol–Gel Method

It is a wet chemical process used to create thin films on metal or glass substrates and produce ceramic compounds. A homogeneous solution is formed by continuously stirring and heating the sol solution. The polycondensation process extracts water from the gel phase, which then becomes powder. In this instance, heating is necessary to produce a powder that is fine and crystalline in nature. The creation of a precursor solution, the application of sol to the substrate using the proper technique, and the thermal treatment of the deposited film are the three steps involved in the formation of thin films via the sol–gel process. The spin coating and dip coating procedures are used in the sol–gel technique to deposit sol on the substrate [27].

Spin coating: To achieve uniform coating, a sol solution is applied to a uniformly rotating horizontal disc. The spin coating process is repeated until the desired thickness for the desired shape and size is achieved. Also, the thickness of the thin film can be controlled by parameters such as the angular concentration, velocity, and viscosity of the sol solution. The deposited film is annealed at a specific temperature after reaching the desired thickness to achieve crystallization [27].

Dip coating: Dip coating involves submerging a substrate in an already prepared sol solution and quickly drawing it out while maintaining precise temperature and ambient conditions. The withdrawal rate, solid content, and gel viscosity are the key determinants of coating thickness [27].

The sol–gel method provides advantages as compared to other techniques, such as coating a large surface, low-temperature processing, controlled thickness, high purity, and good optical quality. The production of composites, hybrids of organic and inorganic elements, and functional materials can all be done using this method [28].

3.3 Microwave-Assisted Synthesis

Microwaves are electromagnetic (EM) radiation with frequencies ranging from 0.3 to 300 GHz. In the microwave-assisted method, there is interaction between the microwave and materials [29]. In this method, moveable electric charges are heated using electromagnetic resonance (EMR) to transfer microwave radiation to the substance. EM energy is converted to thermal energy during this process. This method makes it feasible to create a narrow size distribution of particles. Rapid crystallization occurs in the microwave-assisted method and uniform heating results in homogeneous nucleation. Microwave-assisted synthesis is a quick, energy-efficient, and promising method for the synthesis of functional nanomaterials [29].

3.4 Ultrasonication Cavitation

Ultrasonication cavitation is one of the most promising, quickest, and easiest ways to obtain functional materials. Ultrasonic waves are used in this process to create cavities in a liquid medium. In this method, a composite is prepared after mixing two solutions; after that, a sonicator probe is immersed, and using a pulse controller, ultrasound is applied. The liquid starts oscillating in tune with the sound waves [30]. In this scenario, the tremendous energy held within the cavities is increased by the medium's ultrasonic energy, which also causes chemical excitation both inside and outside of the cavities. This method produces high crystallinity and a narrow size distribution. Solute diffusion as well as nucleation rates increase, and the crystallization process improves as a result of ultrasonic irradiation [28].

3.5 Electrospinning Method

Electrospinning is a quick and easy way to prepare micro – or nanofibers (NFs). A high-voltage power source that is supplied to a liquid solution and a collector that allows the solution to shoot out of a nozzle in the shape of a jet are required for electrospinning manufacturing. After drying, the jet formed fibres that were then placed on the substrate. The NFs prepared using the electrospinning method have broad applications in many fields such as sensing, textiles, biomedicine, and filtration because of their unique structural advantages [28].

3.6 Pulsed Laser Deposition

It is a laser-based physical vapour deposition process in which a high-power pulsed laser beam is focused inside a vacuum chamber to strike a material-to-be-deposited target. It is a very simple approach that consists of a vacuum chamber, a target holder, and a substrate holder [31]. To vaporize the material and deposit thin layers, an external energy source such as a high-power laser is required. The matter is ejected in the form of plasma, which has high kinetic energy. Finally, it settles on the substrate gradually. Pulsed laser deposition is a straightforward, adaptable, thickness-controlled, and low-cost process [25]. A laser beam vaporizes the surface of a target, creating a film with the same composition as the target. Many metals may be deposited in a wide range of gases and pressures, and a single laser can serve multiple vacuum processes [31].

3.7 Sputtering

It is a vacuum-based deposition process. Sputtering is a simple and well-known process in which atoms are ejected onto the surface of a substrate material by bombardment with high-energy particles under high pressure and vacuum. The material to be deposited serves as the cathode in sputtering operations, and the very energetic positively charged ion is assaulted by an electric field on the target or cathodic substance [25]. There are several types of sputtering:

- Magnetron Sputtering
- Reactive Sputtering

Magnetron sputtering: In 1935, Dutch physicist F. Penning was the first to propose employing magnetron sputtering for film deposition. It is used to deposit metals, textile compounds, and several other materials with greater thickness. Magnetron sputtering is very productive and allows for particle size control. For effective functional materials, the effects of the key sputtering parameters (working gas type and pressure, substrate bias potential, target potential, magnetic sputtering system power, distance, etc.) on grain size and film morphology should be considered [32].

Reactive sputtering: This process was originally used to create Ta-N thin films in 1950. It is a common approach for producing microelectronic devices, coated architectural glass, hardware items, and transparent conducting oxides. The deposition rate and film characteristics are heavily influenced by the gas flow rate and partial pressure management. If compound formation on the target surface could be avoided, DC power may be employed for reactive sputtering of insulating coatings [33].

The functional advantage of sputtering is that it simplifies the deposition of refractory metals. However, contamination is more likely with sputtered films [25].

3.8 *Electron Beam Evaporation*

Electron beam (E-beam) evaporation is another vacuum-based physical technique for the creation of thin films of functional materials. An electron beam is produced as a result of the filament transfer across electric and magnetic fields, and it strikes the target before vaporizing it in a vacuum environment [25]. The electron beam is used to heat the material to be deposited. Optimizing the deposition conditions is a potential technique for depositing materials with high crystallinity, controlled stoichiometry, and a high deposition rate. The advantages of E-beam evaporation include its capacity to use numerous sources, its ability to operate at ambient pressure, and its superiority in managing deposition rate [25].

4 Different Functional Materials for Sensor Application

In this session, we have discussed different functional materials for sensor applications, mainly focused on the hazardous gas sensor and optical sensor. The functional materials discussed include metal–organic frameworks (MOFs), quantum dots (QDs), graphene and graphene-based materials, and MXene.

4.1 *Hazardous Gas Sensor*

Various harmful gases are generated from various businesses, including the automotive industry, vehicle exhaust, and the combustion of fossil fuels, among others, as a result of rapid industrialization. Air pollution is a major contributor to public health issues like respiratory ailments as well as significant climatic changes like acid rain and global warming. Table 2 is a list of some dangerous gases, their sources, and their effects. The identification and monitoring of dangerous gases have been elevated to the top priority for safeguarding the environment and human health.

4.1.1 Metal–Organic Frameworks (MOFs)

Air pollution is caused by excessive industrial toxic gas emissions (sulfur dioxide (SO_2), hydrogen sulfide (H_2S), nitrous oxide (NO_x), etc.) has become a global challenge. Because of these pollutants, efficient analysis of atmospheric pollutants is essential [34]. MOFs are perfect for the creation of gas sensors because they have a high specific surface area, a changeable structure, are persistent, and have excellent porosity. MOFs have a number of physical and chemical properties that make them powerful sensing materials, including luminescence, electrical conductivity, and ferroelectricity. For practical application, MOFs are designed to be very stable

Table 2 Hazardous gases, their sources and effects

Hazardous gas	Sources	Effects	References
Nitrogen dioxide (NO_2)	• Automobile exhaust • Industrial combustion • Combustion of fossil • Welding	• Greenhouse effects • Photochemical smog • Damage respiratory system • Acid rain • Threat infection • Lung disease	[36, 40, 66]
Ammonia (NH_3)	• Agricultural activities	• Death (exposure to high concentration) • Cell damage • Respiratory problems	[19, 67]
Hydrogen sulfide (H_2S)	• Chemical industry • Food industry • Decomposition of organic materials • Petroleum refining	• Irritation to eyes • Damage respiratory organs • Even the possibility of death • Causing fire and explosion	[9, 39]
Carbon monoxide (CO)	• Automobile exhaust • Incomplete combustion of fuels	• Unconscious • Headache • Dizziness	[68]

against heat, mechanical pressure, humidity, and chemical conditions under varying acidity and alkalinity [34].

H_2S is a flammable and toxic gas emitted primarily by the food industry, refineries, and paper manufacturers, and it is capable of causing fires and explosions when exposed to fire or high temperatures [9]. According to Wang et al. [9], ZnO/CuO composites, which were produced from bimetal MOFs and serve as a highly sensitive and low-temperature H_2S gas sensor, were created via a straightforward solvothermal route. Figure 5a indicates the solvothermal synthesis of ZnO/CuO composites. The bimetallic Zn/Cu-BTC MOF was prepared by the solvothermal method, and MOF-derived metal oxide (ZnO/CuO composite) was prepared after calcination. The morphology and EDX spectra of pristine and composite materials are shown in Fig. 5b. The ideal operating temperature for gas sensors was determined by testing at temperatures ranging from 20 to 340 °C. By varying molar ratios, the temperature-dependent gas sensing performances of pristine and composite materials are shown in Fig. 5c. The outcome made it very evident that the sensitivity tends to rise with temperature, reach its maximum value, and then fall. The pristine ZnO and CuO-based sensors operate best at 200 °C and 40 °C, respectively, and their sensitivity to 10 ppm H_2S is 134.35 and 23.03 for each material, respectively. The composite sensor reduced the working temperature compared to bare ZnO and enhanced the sensitivity compared to bare CuO, as evidenced by the composite-based sensor's sensitivity of 393.35 at the ideal working temperature of 40 °C. In this work, the sensitivity of the composite sensor is displayed at its highest value by choosing the optimal molar ratio of ZnO/CuO composite, which is 393.35 [9]. For the detection of H_2S gas at room temperature, Ali et al. [35] demonstrated a highly sensitive and flexible MOFs-polymer mixed matrix flexible membrane in their study. Incorporating MOFs as nanoparticles into polymer matrices for sensor membrane fabrication is an effective way to enhance sensor performance. The outstanding results for selectivity, stability, and repeatability show that the sensor membranes are very dependable and have a strong affinity for H_2S when compared to other test gases. The sensor has lucrative industrial uses for monitoring air pollution because of its 1 ppm detection capacity and quick reaction time (8 s) [35].

A typical pollutant gas is nitrogen dioxide (NO_2), which is produced by a variety of automotive engines, industrial processes, and the burning of fossil fuels. NO_2 can lead to significant illnesses such as lung disease, eye irradiation, and throat and nose infections, even at low concentrations. The value of NO_2 gas sensors that function at or near room temperature cannot be overstated. The response, sensing speed, and stability of semiconductor-based gas sensors are good. Cobalt oxide (Co_3O_4)

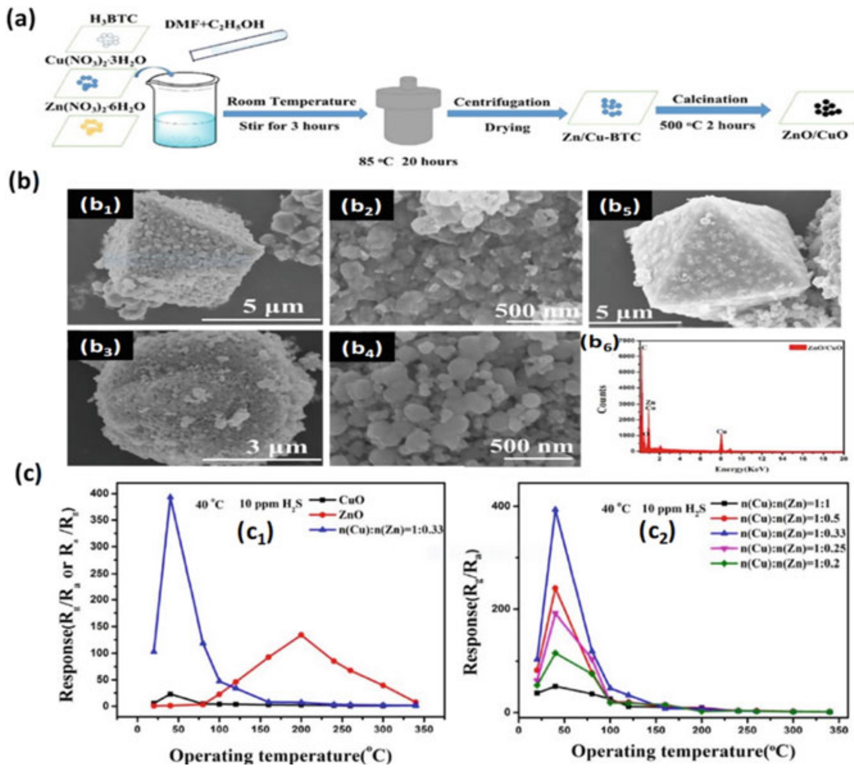

Fig. 5 **a** Solvothermal synthesis of ZnO/CuO composite, **b** FESEM spectra of pristine CuO (b_1–b_2), pristine ZnO (b_3–b_4), and ZnO/CuO composite (b_5) with EDX spectra of ZnO/CuO composite (b_6), **c** Temperature-dependent gas sensing performance of pristine CuO, pristine ZnO, and ZnO/CuO composite (c_1), ZnO/CuO composite with different molar ratios [9]. Copyright (2020) Elsevier

is a p-type semiconductor and a good option for sensing materials due to its high conductivity, non-toxicity, and corrosion resistance [36]. To detect ppb-level NO_2 gas operating at room temperature, Ullah et al. [36] reported highly sensitive Co_3O_4 generated from MOF combined with graphitic carbon nitride (g-C_3N_4) nanosheets (NSs). Due to the formation of p–n heterojunctions (p-type Co_3O_4 and n-type g-C_3N_4), the local electron density of Co_3O_4 has been enhanced, which can facilitate the rapid passage of charge carriers and enhance the gas-sensing capacity. CO_3O_4/g-C_3N_4 achieved quick response and recovery times of 1.06 s and 26.6 s, respectively, for 60 ppm of NO_2 gas concentration. The work suggests new methods for enhancing the sensitivity of gas sensors based on metal oxides that have great potential [36]. CuO_x was reported by Ding et al. [37] by calcining a Cu-based MOF, and the fabricated sensor exhibited a temperature-dependent p–n transition. The study demonstrated that the CuO_x sensor could detect 500 ppb of NO_2 at 25 °C with excellent accuracy. The work revealed that the p-type and n-type reverse sensing signals provide a possible method to improve selectivity at various temperatures [37].

Zhan et al. [38] reported the performance of polyhedral ZIF-8 MOF for the detection of NO_2. Figure 6a shows the steps for forming polyhedral ZIF-8 nanostructures, which were synthesized by the solvothermal method. The molar ratios of metal nitrate to linker were kept at 8:1, 16:1, 32:1, and 64:1, examining how the solvent composition affects the shape and crystal structure of the ZIF-8 nanostructure. Oxygen molecules adsorb on the surface of ZIF-8 MOF nanostructure gas sensors when they are exposed to air. Free electrons are then trapped in the substrate material's conduction band, creating oxygen species ($O_2{}^-$, O^-, $O_2{}^-$) as the conduction channel. Lower temperatures enable the molecular adsorption of the oxygen specified on the surface of metal oxides, but it decomposes into atomic oxygen when exposed to higher temperatures. The following equations can be used to describe the adsorption process:

$$O_2 + e^- \rightarrow O^-_{2(ads)} \quad (1)$$

$$O^{2-}(ads) + e^- \rightarrow 2O^-(ads) \quad (2)$$

$$O_{2(ads)} + e^- \rightarrow O^{2-}(ads) \quad (3)$$

When NO_2 was adsorbed on the surface of ZIF-8, it first interacted with the pre-adsorbed O^{2-} species to generate $NO_2{}^-{}_{(ads)}$, which then entered the conduction band of ZIF-8. This is how the reduction process works.

$$NO_2 + e^- \rightarrow NO_2^- \quad (4)$$

$$NO_2^-(ads) + 2e^- + O_2^-(ads) \rightarrow NO_{(gas)} + 2O^{-2}(ads) \quad (5)$$

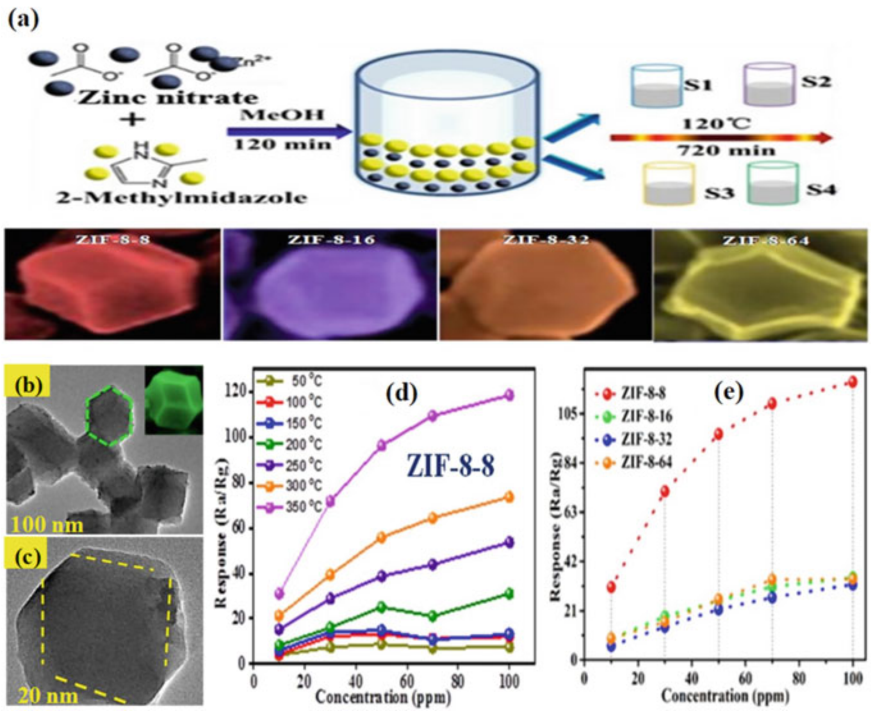

Fig. 6 **a** Synthesis of formation of polyhedral ZIF-8 nanostructures, **b**, **c** TEM images of a single polyhedral ZIF-8-8 nanostructures, **d** Response versus NO_2 concentrations at different working temperature ranging from 50 to 350 °C, **e** Comparison of responses with all four tested ZIF-8 samples versus concentration [38]. Copyright (2021) Elsevier

The gas molecules trapped free electrons from the adsorption of oxygen on the sensor's surface when the manufactured sensor was tested for NO_2, which led to the creation of a significant charge depletion layer on the ZIF material's surface. When a ZIF material is exposed to air again, the surface electrons enter the conduction band and lower the resistance of the sensing material [38]. Figures 6b and c show the TEM results of polyhedral ZIF-8-8, revealing that the particles are nanocrystals with sharp hexagonal facets. Nanomaterials' structural shape has a significant impact on their gas adsorption ability. The size of the specific surface area and the number of adsorption sites in the material are critical factors for strong adsorption. Figure 6d depicts the response versus NO_2 concentration range of gas sensors based on ZIF-8-8 nanomaterial at various working temperatures ranging from 50 to 350 °C. The response increased linearly as the temperature increased, with the maximum response observed at 350 °C. A comparison of responses with all four tested ZIF-8 samples versus concentrations at operational temperatures is shown in Fig. 6e [38].

4.1.2 Quantum Dots

H_2S is a hazardous gas that is produced by industrial processes such as natural petroleum refining, gas processing, cooking ovens, coal chemistry, food processing, and tanneries. For the detection of H_2S toxic gas at low concentrations, special techniques and highly efficient strategies are generally required [39]. Metal oxides have drawn attention as efficient gas semiconducting sensors in recent years because of their speed of response, small size, affordability, simplicity of use, and excellent compatibility with microelectronic processing. SnO_2, although it has widespread use in n-type semiconductors, has the ability to sense nearly all gaseous species. It has serious limitations, including low selectivity and operating at extreme temperatures with low specificity. SnO_2's gas sensing capabilities can be improved in a variety of ways, including by increasing surface area, reducing particle size, and using unique morphologies of structures with a significant specific area [39]. This work investigates the gas sensing properties of the SnO_2 QDs-fullerene (SnO_2 QDs-C60) nanohybrid in order to enhance response and selectivity towards H_2S gas over other gases. Due to the characteristics of fullerenes, including their prominent mechanical properties, chemical stability, and porous structure, the responsiveness of H_2S towards hybrid sensors is improved. In reaction to 70 ppm of H_2S gas, the SnO_2 QDs-C60 hybrid sensor showed the greatest response of 66.0 with a response time of 258 s. According to the study's findings, a nanohybrid sensing material may be a viable option for enhancing gas sensing capabilities and spotting environmental pollutants [39].

NO_2 is a significant air pollutant that causes acid rain and photochemical smog and has an impact on tropospheric ozone. Human endeavors like the burning of fossil fuels, commercial and food manufacturing, welding, and so on emit a significant amount of NO_2. These activities produce a large amount of NO_2, which has a significant impact on human health [40]. For applications requiring gas detection at room temperature, MoS_2 is a potential candidate, but due to the incomplete recovery and limitations of the synthesis technique, MoS_2 gas sensors show drawbacks. Using sputtering on a silicon (Si) substrate, Jaiswal et al. [10] studied CdTe quantum dots (QDs) adorned with MoS_2 nanowarms (NWs), creating a hybrid nanostructure (CdTe QDs/MoS_2 NWs), and evaluated it for the RT NO_2 sensing application. The outcome showed that the hybrid heterostructure was highly selective towards 10 ppm of NO_2 at RT and had quick reaction and complete recovery durations of 16 and 114 s, respectively. The enhanced gas sensing ability may be attributed to the p–n heterojunction and hybrid nanostructure with synergistic effects [10]. Mitri et al. [40] reported RT NO_2 lead sulphide colloidal QDs (PbS CQDs) gas sensors, and the gas sensor device was fabricated by using the drop casting method. QDs-based sensors benefit from features like a large surface-to-volume ratio and high reactivity towards targeted gases. Different pollutant gases, including NO_2, CH_4, CO, and CO_2, as well as various concentrations, have been used to measure the sensor response. Among other air contaminants, the manufactured device was able to selectively detect NO_2. The device demonstrated expected selectivity, repeatability, and full recovery after exposure, as well as response and recovery times of 12 s and 26 min, respectively [40].

4.1.3 Graphene and Graphene-Based Materials

Graphene changes into a p-type semiconductor with a high specific surface area, high mechanical strength, high electrical conductivity, and high thermal stability when exposed to different gases. It is primarily used for photonic devices, fuel cells, biosensors, optical sensors, and hazardous gas sensor applications. When heteroatoms are introduced into graphene, they cause electronic distortion and change graphene properties such as band gap, electrical conductivity, optical properties, and magnetic properties [41]. The focus of contemporary research has switched to graphene-based gas sensors, with scientists concentrating on methods to improve the sensing capabilities of graphene-based materials. The performance of gas sensing is improved by modifying graphene with organic molecules and fabricating it using metal oxides and noble metals.

Chemical vapor deposition (CVD) was utilized by Kumar et al. [42] to create a flexible graphene-paper gas sensor. The room-temperature NO_2 sensing performance of graphene paper is better than that of other reported graphitic sensors. However, the recovery time of the reported sensor was drastically reduced to tens of seconds. The results showed that graphene paper could detect NO_2 at a very low level; however, the stability was not good enough for testing to be done continuously [42]. Local p–n heterojunction by SnO_2 nanofibers and graphene nanosheets for a highly sensitive and selective NO_2 sensor was described by Lee et al. [43]. The NO_2 sensing test revealed that loading an ideal amount of RGO boosted the sensing responsiveness of RGO NSs-loaded SnO_2 NFs by around 20 times. Due to the p–n heterojunction, an efficient sensing response was obtained in this report, and this approach is used to fabricate graphene-based sensors [43].

A high-performance hydrogen sensor composed of graphene and embellished with Pd/Ag nanoparticles was described by Kim et al. [27] utilizing the microelectrochemical system approach. The H_2 sensing performance was greatly improved by the graphene-Pd/Ag nanoparticles. In this instance, graphene offers a route with high conductivity, which is helpful for enhancing H_2 adsorption and sensing. Pd/Ag nanoparticles are effectively disseminated on graphene and serve as the catalyst in H_2 sensing. This promotes quick gas adsorption and desorption kinetics, lowers resistance, and speeds up charge transfer [27].

4.1.4 MXene

MXene has become a hotspot of material science and its potential in sensing applications due to their superior optical characteristics, large surface area, biocompatibility, and high conductivity [44]. Xia et al. [45] described the use of an MXene/WS_2 hybrid for visible-light-activated NO_2 detection at room temperature. WS_2 is a p-type material, and due to its strong electronic interaction, it is sensitive and selective towards NO_2. A visible-light-activated, room-temperature NO_2 gas sensor was developed and utilized in this work. The sensor was comprised of a hybrid sensing film composed of multiple layers of WS_2 nanosheets and $Ti_3C_2T_x$ nanosheets. At ambient temperature, a $Ti_3C_2T_x/WS_2$ hybrid film-based NO_2 sensor demonstrated improved sensitivity, a rapid sensing rate, and complete reversibility. The visible-light activation effect provided by heterostructures could be attributed to the enhanced sensing performance towards NO_2. The hybrid sample responded more strongly than the $Ti_3C_2T_x$ and WS_2 single phases, implying that the heterojunction formed by $Ti_3C_2T_x$ and WS_2 enhanced the hybrid sensing performance [45].

In the production process of nitrogen fertilizer, a leak of NH_3 could occur. Moreover, NH_3 can deplete oxygen throughout the body, which is harmful to human and animal health. As a result, there is a critical need for a low-cost, high-efficiency NH_3 gas sensor [46]. Metal halide amines, carbon nanocones, graphene, and metal oxide semiconductors have all been developed as NH_3 sensing materials. However, high-temperature operation restricts their use. In numerous investigations, 2D MXenes have been used as a gas-sensing material. 2D MXenes have recently undergone extensive research in many applications. NH_3 gas molecules interacted with pure, Hf-doped $Ti_3C_2O_2$, Cd-doped $Ti_3C_2O_2$, and Cd-Hf co-doped $Ti_3C_2O_2$ MXene, according to Li et al. [47]. The outcome shows that doping with the transition metals Cd and Hf enhanced NH_3 adsorption on $Ti_3C_2O_2$'s surface. The detection of NH_3 is a big prospective application for Cd-Hf-codoped $Ti_3C_2O_2$ [47].

Table 3 displays the tabulation of hybrid nanomaterials for hazardous gas sensor applications as well as the full result of this investigation.

4.2 Optical Sensor

An optical sensor is a piece of equipment that may offer optical data, such as reflectance or fluorescence emission, and information about how materials and metal ions interact to modify the intensity and efficiency of quenching. There are numerous optical techniques, including electrochemiluminescence (ECL), surface plasmon resonance (SPR), fluorescence, and photoluminescence (PL) [48].

4.2.1 Metal–Organic Frameworks (MOFs)

MOFs are a distinct family of crystalline solids that have shown potential for many different uses. They are composed of organic ligands and metal cations (or metal clusters). The crystalline structure, high and persistent porosity, and wide range of applications of MOFs are well known. MOFs are preferable to other porous materials like zeolites and carbon-based compounds because of their porous nature. Not only can functional sites be easily immobilized on the porous surfaces for targeted molecule recognition, but the pores of the MOFs may also be systematically adjusted using varied ratios of metal ions and organic molecules. Recently, an intriguing area of research for sensing purposes has been opened up by the luminescence characteristics of MOFs. A molecule can return to the ground state both radiatively and non-radiatively after being promoted to the excited state. The presence of a radiative route

Table 3 An overview of functional materials for hazardous gas sensor application

Hazardous gases	Functional materials	Synthesis route	Gas concentration (ppm)	Response	Operating temperature (°C)	Response/recovery time	References
H_2S	Zn/Cu-BTC	Solvothermal	10	–	40	–	[9]
	SnO_2 QDs-C_{60}	Hydrothermal	70	66	150	4.3 min/140.4 min	[39]
	CNTs/SnO_2/CuO	Sol–gel spin coating	10	4.41	RT	4 min/10 min	[69]
	MoO_3/rGO	Microwave hydrothermal	40	59	110	9 s/17 s	[70]
	MoO_3/rGO	Impregnation	50	4120	160	60 s/120 s	[71]
NH_3	rGO/WO_3	Hydrothermal	100	11	300	–	[72]
	Sn-TiO_2@rGO/CNT	Solvothermal	250	85.9%	RT	99 s/66 s	[73]
	GCs/PANI	In situ polymerization	10	1.30	RT	34 s/42 s	[74]
	rGO/PANI	Chemical polymerization	100	–	RT	36 s/18 s	[75]
	PANI/CNTs	Interfacial polymerization	30	40	RT	18 s/46 s	[76]
	PPy/MWCNT	In situ chemical oxidative polymerization	2000	17.11%	50	34 s/–	[77]
NO_2	CdTe QDs/MoS_2 NWs	PVD	10	–	RT	16 s/114 s	[10]
	CO_3O_4/g-C_3N_4	Chemical method	60	17.83	RT	1.06 s/26.6 s	[36]
	MOF derived CuO_x	Calcination route	500 ppb	76.69%	25	–	[37]

(continued)

Table 3 (continued)

Hazardous gases	Functional materials	Synthesis route	Gas concentration (ppm)	Response	Operating temperature (°C)	Response/recovery time	References
	Polyhedral ZIF-8 MOF	Solvothermal	10–100	118.5	350	113.5 s/115.5 s	[38]
	WO_3/MWCNTs	Bar-coating slurries	5	18	150	87 s/300 s	[78]
	PPy/N-MWCNTs	In situ self-assembly	5	24.82	RT	65 s/668 s	[79]
	SnO_2-$BiVO_4$	Hydrothermal	0.1	0.91%	RT	13 s/9 s	[80]
	MoS_2/SnS	Hydrothermal	25 ppb	–	RT	74 s/140 s	[81]
	ZnO-TiO_2-PANI	Spin coating	20	412	RT	–	[82]

causes the molecule to glow. When exposed to light, the organic ligands' aromatic properties can be excited and result in optical emission or photoluminescence (PL) [49].

Another way that the metal components can contribute is through photoluminescence, which is typically associated with lanthanides or other inorganic clusters. The sources of luminescence in MOFs are often conjugated organic ligands and/or metal ions or clusters, while occasionally adsorbed guest molecules may also contribute to the emission. The luminescence, which can be classified as ligand-to-ligand charge or linker-based luminescence, is greatly influenced by the electrons in these linkers. Both ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) are regularly observed in d10 transition metal-based-MOFs. While MLCT is generally observed in Cu(I) and Ag(I) compounds, LMCT is regularly observed in Zn(II) and Cd(II) compounds [50].

Most importantly, guest molecules can live naturally in LMOFs thanks to their sustainable porosity. In addition to raising the likelihood of guest-host interactions, the guest molecules are pre-concentrated within the pores, which may help with sensitive detection [50]. Sharp emission lines, substantial Stokes' shifts, persistent emission, and high quantum yield are some of the distinguishing features of rare-earth-based MOFs (Re-MOFs). Because their luminescence properties, which heavily depend on the structural details of the coordination environment around the lanthanide ions, are often not quenched by oxygen, rare earth ions have a special affinity for the efficient chemical sensing of analytes [49]. Several sensing applications for the luminous MOFs as sensitive materials exist, including those for temperature, metal ions, anions, small molecules, gases, nitroaromatics, and explosives.

4.2.2 Quantum Dots

Quantum dots (QDs) exhibit quantum processes that significantly enhance optical properties due to their size. It can be created from semiconductors, metals, or carbon-containing materials like graphene, cadmium sulfide, and carbon quantum dots [48]. QDs have been identified as the active component in optoelectronics. Due to QDs' size-dependent bandgap, the emission and absorption spectra can be easily modified during synthesis [51]. QDs have been studied for light-emission diodes for a long time due to their operation stability, solution processibility, high luminescence efficiency, and tenability in emission wavelength [51]. Simple, transportable, and small PbS QDs optical sensors for airborne nitrobenzene (NB) detection were reported by Mitri et al. [51]. The graphic depicts the optical arrangement's schematic. The system is based on the integration of a QD photodetector and a solid-state QD photoluminescent probe on the same substrate. The photons emitted can enter the QD photodetector and generate a photocurrent proportional to the PL intensity [51]. The device was sensitive to NB concentrations between 131 ppb and 1.18 ppm and had remarkable repeatability after several cycles of the NB concentration. During the 70-day testing period, the sensor demonstrated long-term stability and a consistent response to varying humidity conditions [51]. In the field of public security and defence, Wu et al. [52] developed a fluorescence sensor array based on nanofibrous membranes filled with ZnS QDs for an explosives monitoring system [52]. The high surface-to-volume ratio of QDs and the robust permeability of nanofibrous membranes worked in concert for great success in the sensing system.

When compared to other QDs, graphene quantum dots (GQDs) are a very promising sensing material. GQDs have received increased attention as a result of their superior optical, mechanical, electrical, and thermal properties, as well as their excellent biocompatibility, high solubility in a range of solvents, and low toxicity [48]. GQDs are a good material for the application of optical sensors because they have changeable optical properties [53]. Wang et al. [54] successfully increased the fluorescence of GQDs by adding amide and amino groups to detect Fe^{3+} by synthesizing amino-functionalized GQDs (af-GQDs). The computed value for the limit of detection of Fe^{3+} was 0.51 nM, and a significant linear relationship between the ratio of fluorescence intensity and Fe^{3+} concentrations between 0 and 50 M was observed [54]. One of the most dangerous heavy metal contaminants, mercury (Hg), is bad for the environment and human health. The development of an optical sensor based on GQDs for the precise detection of Hg^{2+} has advanced [53]. Research by Qu et al. [53], focused on the simple and environmentally friendly pyrolysis-based synthesis of nitrogen and sulfur-co-doped GQDs (N, S/GQDs). To create a novel fluorescence quenching mechanism, the author of this work chose molecules functionalized with nitrogen and sulfur. The fluorescence spectra of N, S/GQDs, and added 10 and 50 M Hg^{2+} are shown in Fig. 7a. The maximal emission peak of N, S/GQDs underwent a significant fluorescence suppression when Hg^{2+} was introduced. The fluorescence spectra of GQDs and N, S/GQDs are shown in Fig. 7b before and after the addition of 200 M Hg^{2+}, and it is clear that the latter is substantially more quenched by Hg^{2+} than the former. In response to this change in wavelength, a complex between Hg^{2+} and the functional groups of N, S/GQDs is formed. Figure 7c is a depiction of the UV-Vis spectra that were employed to support the complex formation. Last but not least, it was shown that the functional groups of the generated N, S, and GQDs interacted with Hg^{2+} to enhance ion recognition and that the doped N and S significantly contributed to this enhancement [53].

4.2.3 Graphene and Graphene-Based Materials

The 2D carbon compound known as graphene has gained popularity in a variety of academic disciplines, including physics, chemistry, and material science. Its exceptional qualities make it a prime choice for several applications, including energy devices, conductive sheets, and transistors. Due to their significant surface area and high electrical mobility, graphene-based materials like graphene, graphene oxide (GO), and reduced graphene oxide (rGO) have been extensively employed in sensing applications. Graphene is being used to create a lot of gas sensors, chemical sensors, and biosensors. Due to the benefits indicated above, graphene and graphene-based materials are employed in optical sensors; nonetheless, there have been few

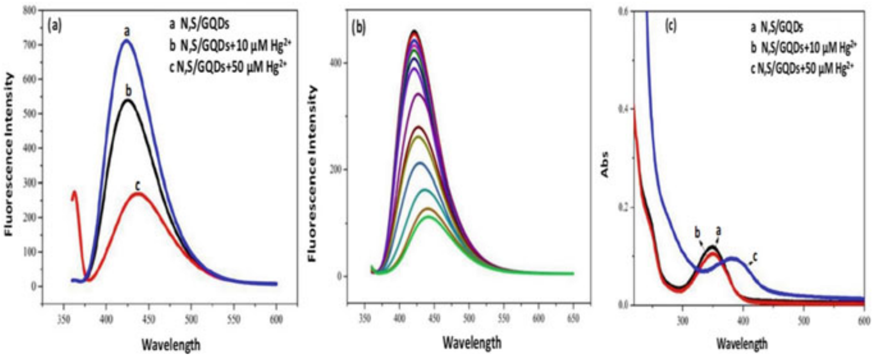

Fig. 7 **a** Fluorescence spectra of N, S/GQDs and added 10 and 50 μM Hg^{2+}. **b** Fluorescence spectra of GQDs and N, S/GQDs before and after added 200 μM Hg^{2+}. **c** UV–Vis spectra of N, S/GQDs and added 10 and 50 μM Hg^{2+} [53]. Copyright (2019) Elsevier

publications on graphene-based optical fiber sensors. Graphene's unique chemical, optical, and morphological properties make it useful for optical sensing. Optical fiber sensors use light intensity measurements to detect phenomena including reflection, absorption, and transmission.

At ambient temperature, the optical gas sensing properties of GO as well as rGO were reported by Kavinkumar et al. [55]. The GO was created from graphite using a chemical oxidation technique, then thermally reduced into GO110 and GO220. Using a white light source and a fiber-optic experimental setup, the optical sensing capabilities were investigated. The variation in output light intensity was continually measured for each concentration after passing the vapor for 10 min. The GO, GO110, and GO220 coated fiber optic sensors were used at RT to find ammonia, ethanol, and methanol vapors. The GO sensor detected vapors of ammonia, ethanol, and methanol between 0 and 500 ppm with sensitivities of −0.32, −0.26, and −0.20 counts per ppm, respectively. According to the results, RT may manufacture flexible electronic devices and fiber optic sensors with greater sensitivity using GO [55].

Khalaf et al. [56] reported a plastic optical fiber (POF)-coated graphene/polyaniline composite for ammonia detection. The drop-casting method is used to deposit graphene/polyaniline nanocomposite onto a side-polished POF. The absorption performance of the suggested sensor improves linearly with the increase in ammonia concentration when it is exposed to various concentrations of ammonia, ranging from 1 to 0.25% at ambient temperature. The synthesized graphene/polyaniline nanocomposite had response and recovery times of 24 and 71.8 s, respectively, illuminating the enormous potential of the POF for creating gas-sensing devices [56]. According to Tian et al. [57], violet light illumination allows for the customization of the absorption properties of methyl blue-functionalized reduced graphene oxide (MB-rGO) that has been placed on microfiber (MF). In light of the findings, it can be said that the MB-rGO has great potential for use in photonic applications, including fiber-optic sensors and other photonic devices [57].

4.2.4 MXene

MXene is the fastest-growing 2D material family, with exceptional electrical, electronic, and mechanical properties. MXene's optical response is also affected by its number of layers. MXene materials have the advantage of having high optical transparency as well as good electrical conductivity, which is required for optical and optoelectronic sensors, solar cells, photocatalysis, and photovoltaic applications [44]. MXene is easily converted into quantum dots, nanosheets, and MXene-based composites. For biosensing and imaging applications, MXene quantum dots (MQDs) can be easily functionalized with natural biomaterials [58]. Lu et al. [58] reported Ti_3C_2 MQDs for optical sensor applications. In this work, Ti_3C_2 MQDs are synthesized by a solvothermal method utilizing bulk Ti_3C_2 as the starting material. Ti_3C_2 MQDs are prepared and applied under high pressure, as shown in Fig. 8a. To investigate the piezoelectric effect in the Ti_3C_2 MQDs, a symmetric diamond anvil cell was used for all in-situ high-pressure tests, and the author looked at how pressure affected their luminescence [58]. Figure 8b shows the SEM image of the as-prepared bulk Ti_3C_2. The PL spectra of Ti_3C_2 MQDs as well as the UV-vis spectra of Ti_3C_2 MQDs at various pressures are shown in Fig. 8c and d. The fluorescence emission of Ti_3C_2 MQDs demonstrated a gradual red shift as the applied pressure increased. After two cycles of compression and decompression, there is no change in the PL spectra's variations about pressure. The outcome showed that these Ti_3C_2 MQDs white emission is extremely stable at high pressure, and that pressure also permits the change from cold to warm white emission [58].

MXene systems have been used to create high-performance optical sensors. MXene is synthesized in monolayers or multilayers as MXene nanosheets (MNSs), which are typically ultrathin and flat [59, 60]. MNSs are excellent optical sensing probes due to their large surface area, good hydrophilicity, non-toxicity, mechanical stability, and biocompatibility. Many fluorophores, including organic dyes, CDs, and PQDs, can be quenched by MNSs [61, 62]. Colorimetric sensors are becoming increasingly popular due to their ease of use, low cost, and high selectivity or sensitivity. Colorimetric sensors have also been developed using MXene nanocomposites. Wang et al. [63] reported Ti_3C_2 MXenes for the detection of Ag^+ ions using nanoplasmonic strategies. The absorbance of the solution and the concentration of Ag^+ had a linear relationship. Li et al. [64] reported Ti_3C_2/CuS nanocomposites for cholesterol detection in a linear range of 10–100 μM and a detection limit of 1.9 μM in another study. Zhu et al. [65] reported an effective and selective fluorescent turn-on nanosensor for glucose detection based on Ti_3C_2 MNSs combined with red-emitting carbon dots (RCDs). Ti_3C_2 MNSs were also proposed for monitoring blood glucose levels in a linear range of 0.1 to 20 mM. The result revealed that the fabricated sensor had excellent selectivity towards glucose analysis and could be used as a platform for glucose sensing in clinical diagnostics [65].

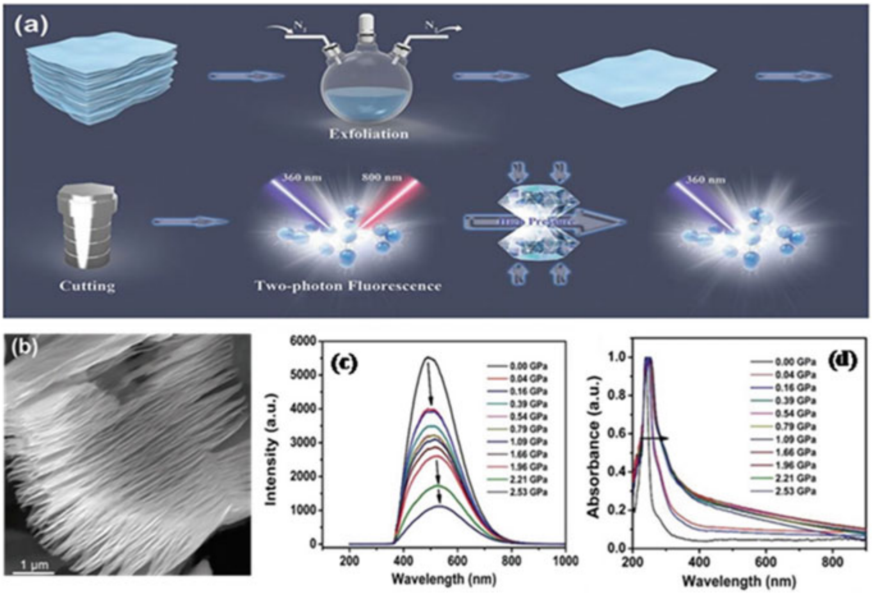

Fig. 8 **a** Preparation and application of Ti_3C_2 MQDs under high pressure, **b** SEM image of as-prepared bulk Ti_3C_2, **c** PL spectra of Ti_3C_2 MQDs with increasing pressure, **d** UV–vis spectra of the Ti_3C_2 MQDs at selected pressure [58]. Copyright (2019) Wiley

5 Conclusion

Research on advanced functional materials, which have novel properties and improved performance, is expanding quickly and cutting across many different disciplines. Work on functional materials for sensor applications is ongoing at numerous research institutions worldwide. The researchers used novel approaches and unconventional functional materials. The study focused mainly on two sensors, which are hazardous gas sensors and optical sensor-based functional materials. In the current environment, we have outlined the requirement for functional materials for applications involving sensing while utilizing nanomaterials like MOFs, QDs, MXene, graphene, and materials derived from graphene. Many studies on the sensing behavior of these nanomaterials for a variety of gases, including H_2S, NO_2, CO_2, LPG, NH_3, and others, have been published in the past several decades. Researchers also changed the structure of the nanomaterials by adding additional dopants, known as functional materials, to improve the sensor response. This synthesis of nanomaterials, which induces some structural defects and extra vacancies on the parent structure's surface area, enables the adsorption of more gas molecules on the active surface. We were unable to cover all the improvements in the sensing performance of several advanced functional materials, despite the abundance of exciting research articles.

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Low-Dimensional Advanced Functional Materials as Hazardous Gas Sensing

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Abstract The intriguing structural, chemical, physical, and electrical properties of low dimensional advanced functional nanomaterials have been proven to be promising ultra-sensitive gas detectors. Low-dimensional materials (i.e., 0D, 1D, and 2D) have an extraordinarily enhanced surface-area-to-volume ratio, revealing a great number of interaction points with molecular analytes. Gas sensor built from these materials responds swiftly and reliably to slight external perturbations on sensing channel material via electrical transduction, demonstrating fast response/recovery, specific selectivity, and excellent stability. In this chapter, we thoroughly discuss the capabilities of gas sensing in the area of sensitive detection of dangerous gases utilizing a range of low-dimensional sensing materials and hybrid combinations. The objective is to obtain a better knowledge of the material design of various nanostructures and to give appropriate design recommendations to help enhance the device performance of nanomaterial-based gas sensors.

Keywords Low dimension materials · Aspect ratio · Hazardous gas sensing

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1 Introduction

Gas sensors are widely used in many different industries. Many gas sensors are required in the civilian sector to identify dangerous chemicals and gas sensors are also cost-effective and functional instruments for quick medical diagnosis [1, 2]. Moreover, gas sensors are crucial for detecting bombs for anti-terrorism purposes and monitoring the quality of the atmosphere. There are many different kinds of gas sensors, including optical sensors, electrochemical sensors, Schottky diode sensors with field-effect transistors (FETs), chemo-resistive gas sensors, and others [3–5]. The demand to create next-generation electronic gadgets that are wearable, lightweight, portable and is growing as a result of recent advancements in internet of things (IOT) technology [6]. The lock and key kind of smart sensors that monitor a single stimulus are giving way to multiplex types that detect complex stimuli with great precision when combined with artificial intelligence technologies [7]. With the development of technology, there is an increase in demand for critical sensing materials that can gather data from the environment, such as temperature, humidity, atmosphere, water quality, light, and movement [8, 9]. There are various sensors fabricated by using metal oxide having good response toward hazardous gas are reported in previously published articles [4, 10–17].

Small molecules and low dimensional-based organic compounds have several benefits, including high stretchability, biocompatibility, and adaptability for low-cost mass manufacturing. The ability of features like adjustable molecular interaction, band-gap, and modulus to be changed by molecular structural alteration that confers sensitivity to the target stimulus is a particularly intriguing feature of low-dimensional materials for smart sensors [18]. Moreover, these low-dimensional materials may be functionalized by other materials while preserving their special features due to their compatibility with a variety of components. An example of hazardous gas sensing could be a gas sensor that is designed to detect the presence of carbon monoxide (CO) in the air. Carbon monoxide is a colorless, odorless gas that is highly toxic and can cause serious health problems or even death if inhaled in high concentrations. A gas sensor that is specifically designed to detect CO can be used in a variety of applications, such as in homes, offices, or industrial settings where CO may be present as a result of incomplete combustion or other processes. The gas sensor would be able to detect even very low levels of CO and trigger an alarm or other alert system to warn people in the area of the danger and prompt them to take appropriate action. This type of gas sensor could be a life-saving device, as it would allow for early detection of CO and help prevent exposure to this hazardous gas.

The high surface-to-volume ratios (S/V), formation of more active sites by reducing the size of low-dimensional materials make them better at gas sensing than bulk materials. Nevertheless, the nanomaterials had a significant advantage over the criteria that determine gas sensing performance. For instance, 0D nanomaterials, which have more active sites and a high S/V, are superior in terms of receptor function and usefulness, but their transducer function is ineffective. Contrarily, 1D and 2D nanomaterials are capable of exceptional advantage in the transmission of electrical signals and irresistible benefits in various devices because they may span two electrodes of a specific size from resistive and FET devices [19, 20]. One way to create nanocomposites that take full use of their benefits is by functionalizing these nanomaterials. Moreover, the aggregation of 0D nanoparticles can be prevented with the use of 1D or 2D nanomaterials. Nobel metal NPs are examples of 0D nanomaterials that are not ideal for the fabrication of sensor devices. However, they can still provide active sites to specifically catalyze or absorb certain gas molecules. Selectivity may be enhanced by using these heterojunction nanomaterials. Furthermore, heterojunction between two different material systems is helpful for gas sensing [21, 22].

The functionalization of 0D nanomaterials, such as nanocrystals, nanoparticles (NPs) and quantum dots (QDs), on a variety of 1D or 2D backbones, is covered in this chapter. Although 0D functionalization has been studied and numerous outstanding studies have summarized the creation of 1D and 2D nanomaterials for the gas sensors. There hasn't been much attention paid to the function of 0D nanostructures in 0D-1D and 0D-2D nanocomposites. A schematic of an overview of various heterostructures using 0D, 1D, 2D, and 3D materials including 2D nanostructured materials utilized for gas sensing applications has been shown in Fig. 1. In this chapter, we focus more on how to deposit 0D nanomaterials on 1D or 2D backbones as well as how 0D-1D and 0D-2D nanocomposites perform in terms of gas sensing. Lastly, gas sensing capabilities of 0D-1D and 0D-2D nanocomposite are presented along with their advantages and disadvantages.

2 Different Kinds of Gas Sensors

2.1 OD Gas Sensors

In comparison to the predominate MOSs materials, 0D noble metals are not as frequently researched for gas sensors. To selectively detect specific particular gases, only a few metals may be utilized as main materials. The high H_2 solubility of palladium (Pd), for instance, has been claimed to make it a suitable noble metal sensing material for H_2 detection.

The production of Pd hydride (PdH_x) during the H_2 adsorption process serves as the basis for the sensing mechanism. The Pd hydride (PdH_x) that forms during the H_2 adsorption process provides the insights for the sensing mechanism. As Pd's d-states

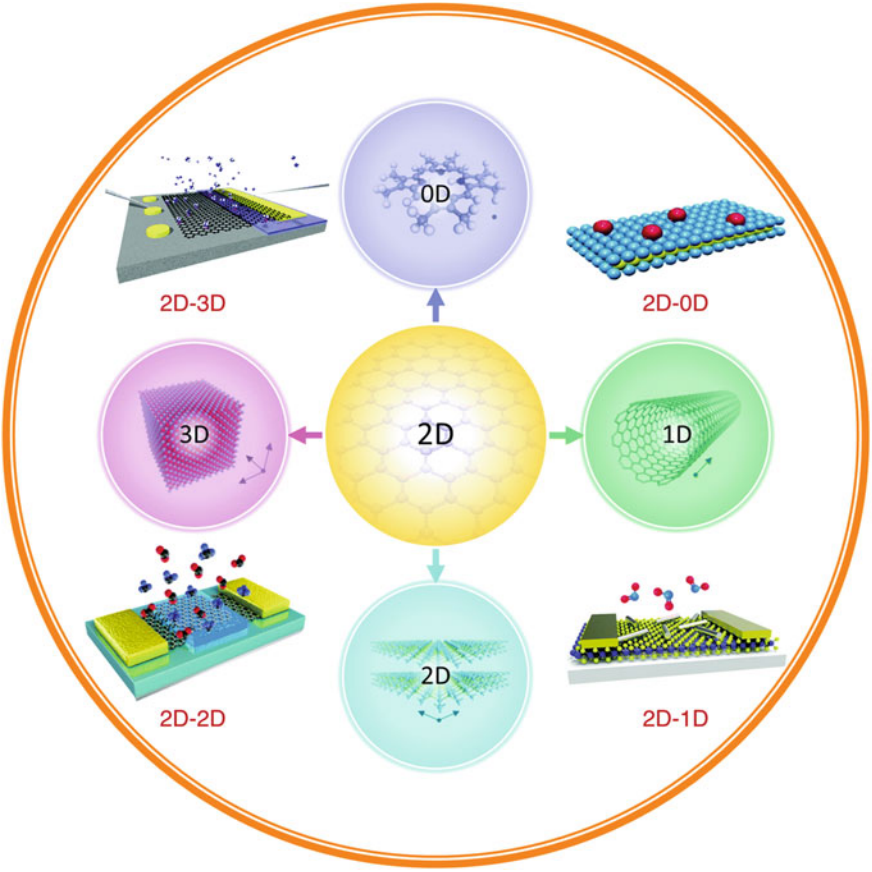

Fig. 1 Overview of various heterostructures using 0D, 1D, 2D, and 3D materials including 2D nanostructured materials utilized for gas sensing applications [23]. Copyright (2019) Royal Society of Chemistry

are gradually filled with electrons, PdH_x is created after which further H_2 adsorption is prevented [24]. A Pd nanopattern H_2 sensor with very sensitive detecting capabilities was described by Cho et al. However, in the majority of cases, the other semiconducting materials were doped or loaded with 0D noble metals as additions to increase their sensitivity or selectivity in accordance with the electronic sensitization outlined by Yamazoe and Morrison et al. [25]. The addition of noble metal can increase the number of active sites for gas molecule adsorption, provide paths for reactions that would lessen activation, or regulate Fermi levels to create Schottky barriers. The most often mentioned noble metal additions for gas sensors right now are Au, Ag, Pd, and Pt. The usual characteristics of these noble metals are listed in Table 1. $CuO/Cu_2O/Ag$ based gas sensor was made by Choi et al. using a novel top-down lithographic technique. Oxygen may be adsorbed and transported on the surfaces of CuO/Cu_2O by the inclusion of the noble metal Ag. The sensor's sensitivity to acetone was greatly increased ($R/R_a = 8.0$, 0.125 ppb). Excellent CO sensing capabilities were reported for sensors based on WO_3/Pt nanocomposites at low working temperatures. The WO_3 matrix might be chemically and electrically sensitized by the partly oxidized Pt nanoparticles to increase sensitivity and selectivity towards CO. According to recent study findings, 0D bimetallic nanoparticles exhibit special physics-chemical features that set them apart from their monometallic compounds. For detecting HCHO Ag@Pt@ZnO-based MEMS gas sensor developed by Xu et al. [26]. The core–shell nanostructure of the Ag@Pt nanoparticles has a pentagram shape and different atomic ratios (Ag, $Pt_{20}Ag_{80}$, $Pt_{40}Ag_{60}$, $Pt_{60}Ag_{40}$, $Pt_{80}Ag_{20}$, and Pt). By having ppb level LOD, the sensors using $Pt_{60}Ag_{40}$ as the catalyst had the best adsorption capability towards HCHO. HCHO is oxidized to HCOOH at low temperatures, and at high temperatures, this process is translated into CO_2. The decorating of various bimetallic alloy nanoparticles (AgAu and AgPt) on the surfaces of ZnO:Ag might alter the selectivity for gas sensors. Calculations using density functional theory revealed that Ag_5Au_5/ZnO:Ag is best for detecting VOCs and Ag_9Pt/ZnO:Ag for detecting H_2. Even though these 0D nanomaterials have certain benefits, they have extremely strong van der Waals attraction makes the aggregation between the nanoparticles visible. Low sensitivity or a slow response time will result from the thick sensing film's interference with the sensing reaction. The pursuit of increasingly sensitive sensors has therefore been the driving force behind high dimensional nanomaterial research's ongoing advancement. The comparison of the gas sensing response of sensors by using different nanocomposite based on 0D nanomaterials has been shown in Table 1.

2.2 1D Gas Sensors

Two dimensions exist within the nanoscale length scale and make up the category of materials known as 1D nanomaterials. Carbon nanotubes and MOSs with different morphologies have been used as a sensing materials from last few decades. This section introduces a few recent developments for gas sensors in 1D semiconductor nanostructures along with a description of the sensing process. The schematic of the methods used in the creation of one-dimensional (1-D) nanomaterials and the uses of resistive gas sensors built on 1-D nanomaterials has been shown in Fig. 2.

2.3 MOS Based Nanostructures

Because of its extremely high surface-to-volume ratio, high porosity, and distinctive electrical characteristics, MOSs are extensively investigated as sensing materials. These 1D nanomaterials, such as nanowires, nanorods, nanotubes, and nanofibers have appealing topologies and morphologies. As reported in previously published

Table 1 Literature review on the gas sensors by using different nanocomposite based on 0D nanomaterials

Material	Gas	Operating temperature	concentration	Response	References
Al–Mg/ZnO	H_2	250	2000	70	[27]
CdO/ZnO	n-Butanol	300	200	148.6	[28]
$LaFeO_3$–Cl_2	Ethanol	136	200	79.2	[29]
Pt–SnO_2	H_2	350	100	56.5	[30]
$TiO_2/SnO_2/WO_3$	NH_3	200	100	61.5	[31]
Fe_2O_3–PANI	NO_2	RT	20	229	[32]
$LaSrCoO_3$	Acetone	RT	50	37.9	[33]
SnO_2/Pt/Pd	LPG	200	1000	89	[34]
NiO/WO_3	H_2S	100	10	15.03	[35]
Ag–$LaFeO_3$	Xylene	125	10	16.76	[36]
Cu–$ZnFe_2O_4$	H_2S	RT	5	37.9	[37]
Pt–In_2O_3	Acetone	150	1.56	18	[38]
Au–SnO_2	H_2	400	1	1.09	[39]
Pd–$SmCo_2FeO_3$	Acetone	160	1	15.85	[40]

article, well-ordered SnO_2 nanorods were produced using the glancing angle deposition technique and employed as sensing materials. The response of the SnO_2 nanorod-based gas sensors to 5 ppm NO_2 at 20% relative humidity was greater (6000 times) than that of the SnO_2 thin films. Lim et al. synthsized 1D nanofiber patterns made of metal oxides (In_2O_3, Co_3O_4, and NiO) using near-Feld electrospinning. The designs might be created using this technique as grids, diamonds, and hexagrams as needed. When compared to their thin film equivalents, the manufactured gas sensors likewise demonstrated very high responsiveness to trimethylamine.

2.4 Carbon Nanomaterials-Based Gas Sensing

The most popular target gases for SWCNT-based sensors are NH_3 and NO_2, which act as an electron donor and acceptor, respectively, and NO_2 with an unpaired electron. In other words, the electron is transferred from SWCNTs to NO_2 and NH_3 may donate electrons to SWCNTs, resulting in changes in sensor resistance. The detecting capabilities of SWCNT-based gas sensors at RT were described by Kong et al. [42]. It was found that the conductivity visibly increased too much in just 10 s when the sensors were exposed to NO_2. In terms of the NH_3 sensing abilities, the conductance reduced by almost 100 times in just 2 min following the introduction of a 1% NH_3. However, SWCNT-based sensors have a very low recovery time. At 200 °C, the recovery time for 200 ppm of NO_2 was around 1 h.

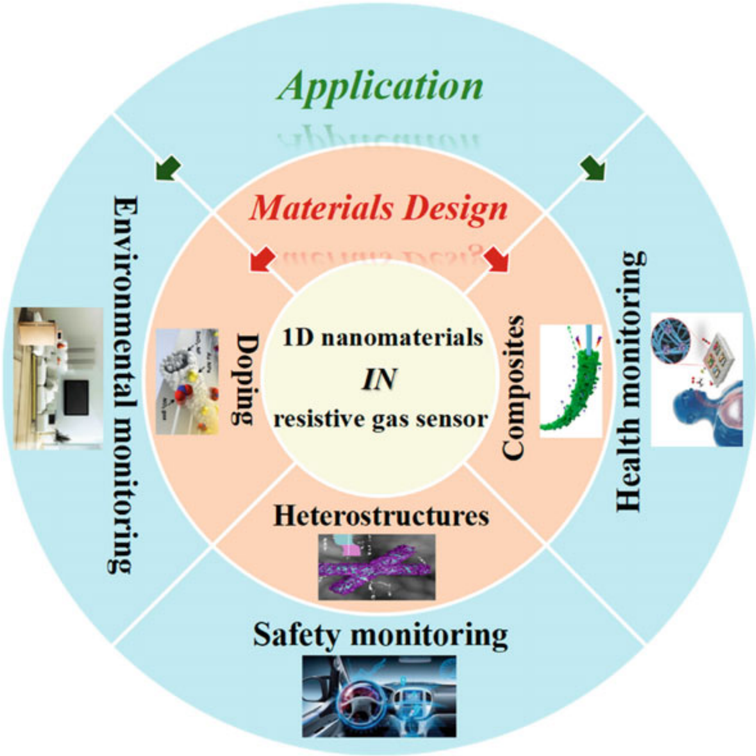

Fig. 2 The methods used in the creation of one-dimensional (1-D) nanomaterials and the uses of resistive gas sensors built on 1-D nanomaterials [41]. Copyright (2021) MDPI

SWCNTs have a lot of potential as RT gas sensors, but their poor sensitivity and slow recovery time prevent them from being widely used. To improve the surface responses for additional target gases, surface modification has been used. To detect cyclohexanone and nitromethane, Schnorr et al. [44] created sensor arrays based on SWCNTs functionalization. Thus, by introducing different gases, sensors based on SWCNTs may detect particular analytes at room temperature. NO and NO_2 were detected at RT using sulfonated SWCNTs. The sensors showed high NO and NO_2 sensitivity in the 40–800 ppb concentration range. The electron-rich sites created by the lone pair of electrons from the S or O atoms in the sulfonic group $–SO_3H$ on the surface of SWCNTs can then be used to adsorb the electron-withdrawing oxidizing molecules (NO and NO_2). So, SWCNTs create large hole charge carriers, which causes the sensor to respond.

Some concentric SWCNTs combine to form MWCNTs. MWCNTs have a diameter that ranges from 2 to 80 nm. Numerous studies concentrated on the improvement of sensing abilities for MWCNTs through surface functionalization as shown in Fig. 3. The comparison of the gas sensing response of sensors by using different nanocomposite based on 1D nanomaterials has been shown in Table 2.

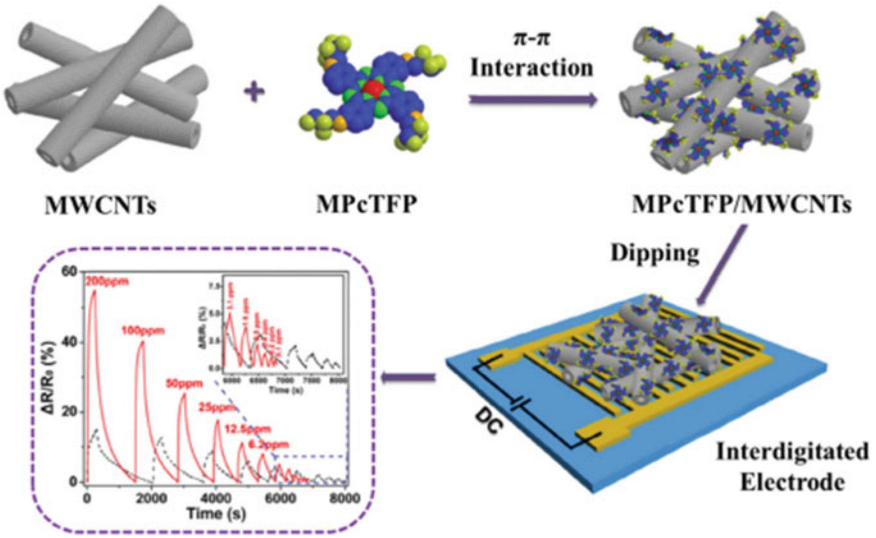

Fig. 3 Graph illustrating the hybrid MPcTFP-MWCNT sensor device [43]. Copyright (2014) Elsevier

For instance, it has been shown that hydroxyl-functionalized MWCNTs can detect NH_3 at RT. The ambient air did not affect the sensor responded to NH_3. Wang et al. reported a NH_3 sensing system has been designed by employing PANI-MWCNT composite thin film. The innovative NH_3 sensor based on carbon nanomaterials demonstrated responses of 10% at 10 ppb of NH_3, quick response/recovery time, and strong anti-bending ability. The increased active sites for adsorption and desorption of PANI–MWCNTs composites enhanced NH_3 sensing capabilities. The preliminary results of the human-breathed NH_3 test indicated potential uses in the monitoring of human kidney health.

2.5 2D Gas Sensors

Due to their superior chemical, physical, and electrical capabilities, 2D materials have just begun to emerge as sophisticated functional nanomaterials. The physical characteristics of several 2D materials, such as work function, bandgap, electro-conductivity, and thermal conductivity have been compiled by Jeong et al. [63]. In comparison to traditional bulk materials, the 2D material design process is more versatile due to ultra-low thickness and even atomically thin layered structure.

Table 2 Literature review on the gas sensors by using different nanocomposite based on 1D nanomaterials

Material	Gas	Operating temperature	Concentration	Response	References
Ag/MWCNT	Acetone	RT	800	3.43	[45]
SnO_2–CuO/Ag	NO_2	RT	20	142	[46]
Fe_2O_3–MoO_3	Xylene	233.5	100	22.48	[47]
Co_3O_4/SWCNTs	H_2S	250	100	500	[48]
MWCNTs/Co_3O_4	Acetone	120	100	5.1	[49]
Ag/SWCNTs	NH_3	RT	62.5	31	[50]
ZnO	NH_3	RT	400	7.29	[51]
SnO_2/In_2O_3	Formaldehyde	375	50	18.9	[52]
Ag-SnO_2/PANI	LPG	160	1000	67	[53]
Au/SWCNTs	NH_3	40	20	110	[54]
Pt–Cr_2O_3–WO_3	Xylene	325	10	74.3	[55]
ZnO–MWCNTs	NH_3	RT	10	1.022	[56]
PANI–ZnO	NO_2	RT	20	611	[57]
SnO_2ZnO	NO_2	70	20	1578	[58]
ZnO/SWCNTs	NO_2	RT	5	7.14	[59]
Ag/Pt/$W_{18}O_{49}$	Triethylamine	240	2	20.28	[60]
TiO_2–SnO_2–TiO_2	Acetone	280	1	13.3	[61]
$CsPbl_3$–SnO_2/ MWCNTs	NH_3	RT	0.2	39.2	[62]

2.5.1 Oxide Heterostructure for Gas Sensing

Various nanostructures with different geometries, including nanosheets, nanoplates, and nanodisks, may be created using 2D MOSs. In addition to these conventional morphologies, the unique 2D shape is ideal for crystal engineering, which has the benefit of exposing active facets primarily for MOSs. Actually, van der Waals interactions during the manufacturing process lead 2D nanomaterials to naturally congregate. Surface area and porosity will decrease as a result of this stacking issue. To achieve excellent gas accessibility, 2D MOSs were skillfully turned into ultrathin nanomaterials with strong mesoporosity in addition to crystal facet engineering. Different method was used to effectively create several 2D MOSs, including SnO_2, ZnO, Co_3O_4, SnO_2/ZnO, and SnO_2/Co_3O_4. Numerous mesopores and a high surface-to-volume ratio were obtained by the sensing layer. SnO_2/ZnO and SnO_2/Co_3O_4 sensors made of heterogeneous metal oxide nanosheets show exceptional detecting abilities toward different kinds of gases.

2.5.2 Graphene-Based Gas Sensing

Covalent bonds between atom-thick sp^2-hybridized carbon atoms give graphene its hexagonal honeycomb lattice structure. Another carbon-based allotrope with a 2D planar surface, graphene, is more flexible than 1D CNTs, making it easier to manufacture for use in electrical devices. High electron mobility and large accessible specific surface areas are some of its favorable physical, chemical, and structural characteristics. Graphene-based sensors, including GO and reduced graphene oxide (rGO), have been extensively investigated in the past several decades for use in sensing. More research was done on graphene derivatives thereafter to increase target gas adsorption capability. The numerous functional groups and defects may be created in the GO or rGO by various methods, providing large active sites to the sensor for the adsorption of different gases.

3 Maxene-Based Gas Sensing

Recently, MXene-based gas sensors have been developed from last few years. Since the MXene family has revolutionized several fields of material science and engineering. A flexible gas-sensing system based on $Ti_3C_2T_x$ nanosheets was developed by Lee et al. in 2017 to detect a variety of polar gases at ambient temperature, including ammonia, methanol, ethanol, and acetone. The manufactured MXene sensor showed that, for 100 ppm of methanol, ammonia, and ethanol the average gas response of $Ti_3C_2T_x$ was 21%, 14.3%, 11.5%, and 7.5% respectively. The $Ti_3C_2T_x$-based sensor displayed the highest response to ammonia due to its high adsorption energy. As one might anticipate from an MXene sensor's sensing mechanism. Although $Ti_3C_2T_x$ is technically regarded as metallic, when produced with functional groups like hydroxyl and oxygen, the band structure has a semiconducting characteristic that enables gas detection in a chemiresistive sensor. The $Ti_3C_2T_x$ MXene film resistance increased when various polar gases (reducing gases) were injected, and it decreased when these gases were removed, demonstrating a p-type sensing behavior. In further detail, electron donor or reducing gas molecules contribute electrons to the $Ti_3C_2T_x$ film when they are adsorbed on the active sites of $Ti_3C_2T_x$ nanosheets (containing surface defects or charged functional groups). As a result, the $Ti_3C_2T_x$ film's predominant charge carrier concentration drops, increasing the sensing film's resistance.

4 Applications of Gas Sensors

4.1 Environmental Monitoring

An urgent issue facing the entire world is ambient air pollution, which poses a major risk to both the environment and human health. The concentration of air pollutants (SO_2, NO_x, CH_4, CO_2, CO, etc.) is relatively high, and it is strongly linked to a number of major environmental issues, including acid rain, global warming, photochemical smog, and others. Major environmental safety bodies have developed standards for the permissible levels of human exposure to certain gases. Monitoring these toxic and dangerous gas concentrations is crucial for a better living environment. A crucial component of the apparatus for gas detection is a gas sensor. The most often used and reported sensing materials for the detection of VOCs, CO, NH_3, NO_2, H_2S, etc., are MOSs. The gas sensing performances, particularly the sensitivity and detecting speed, maybe successfully improved by adjusting the composition and creating the structure of materials.

4.2 Breath Analyzer

Predictive, preventative, personalized, and participatory medicine, or "4P" medicine, sets higher goals for the diagnostic toolkit. Using gas sensors to analyze exhaled breath samples offers a major development in the detection and treatment of illness. Human breath samples include thousands of VOCs and a wide variety of gases, including N_2, O_2, CO_2, H_2O, a few inert gases, and many others. Among these, trace VOCs may serve as the biomarkers for particular disorders. The gas sensors for illness detection still have several drawbacks. The fluctuation of temperature and humidity might also cause issues with stable analysis. Therefore, it is difficult to create gas-detecting devices that are very sensitive, adjustable, moisture-resistant, and stable only by designing the sensing materials. Superior sensing technologies will likely be used in conjunction with sensor arrays, pattern recognition, and classification algorithms. Despite extensive study over a two-decade period, the majority of breath sensors remained in the lab. Without a doubt, more work has to be done to reach actual medical applicability. Medical illness prevention and diagnosis will be revolutionized by precise, quick, hand-held gas-sensing devices, which can significantly improve human health.

4.3 Wearable Electronics

In order to monitor a person's surrounding microenvironment, wearable sensors are sensing instruments that can achieve conformable attachment to the skin or textiles. A top-notch wearable gas sensor should be able to send accurate gas information signals while never interfering with regular movement. The portable wearable sensors are better and simpler to combine with soft interfaces than conventional electronic equipment built on rigid substrates. Due to this, both the functionality of sensing materials and the design of sensing devices are under more scrutiny. The trend of diversification has led to the development of wearable flexible gas sensors. However, to promote the use and continued development, the restricted sensitivity and selectivity for monitoring environment gases need still be enhanced. To stimulate practical use and ongoing development, it is still necessary to enhance the restricted sensitivity and selectivity for monitoring environmental gases. Additionally, there is a considerable need for reliable instruments for environmental monitoring systems.

5 Conclusion and Future Outlook

The sophisticated gas-sensing nanomaterials, which range from 0 to 3D, have been outlined in this chapter. These materials include noble metals, MOSs, TMDs, carbon-based materials (CNTs and graphene), g-C_3N_4, MXenes, and their composites. Due to their great sensitivity and quick reaction times, MOSs are acknowledged in these papers as the leading sensing materials for gas devices. In brief, we anticipate that this study will offer a thorough analysis and synopsis of earlier contributions for gas sensing materials and their applications. Gas sensors are expected to significantly improve human productivity and quality of life. Future high-performance commercial gas sensors will benefit greatly from major technological advances in sensing materials and equipment.

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Advanced of Chalcogenides Based as Hazardous Gas Sensing

Vidya Spriha Kujur, Girish Wadhwa, Kedar Singh, Shehreen Aslam, and Rahul Kumar

Abstract In this twenty-first century, world's ecosystem has been heavily contaminated with various hazardous gas molecules *via* anthropogenic activities and naturally occurring unbalanced processes. Therefore, it is quite crucial to develop sensors for the detection of harmful gas molecules, for which various gas sensors have been utilized to monitor the environment, ensure public safety, address health concerns, to control chemical production, agriculture and medicine applications. The chalcogenides nanostructure-based gas sensors have gained great attention to recent modern sciences as well as alternative to the most promising materials emerging with a variety of potential applications due to owing excellent sensitivity, high selectivity, material design compliances, and great safety characteristics. The nanostructure has quite significant physical and chemical properties than their bulk counterparts due to their enormous surface area to volume ratio, quantum confinement, enlarged band gap, surface defects or dangling bonds, binding sites, etc. Consequently, it has been observed that the chemisorption and physisorption process is significantly influenced by nanostructure creation on the film surfaces, gas type's grain sizes, and operating temperatures. This chapter covers the gas sensors based on nanostructured chalcogenides, its attributes and development.

Keywords 2D materials · Pollutant gas · Chalcogenides nanomaterial · Gas sensors

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1 Introduction

Gas sensors have become important in our lives because they can be used to monitor environment pollutants or detect toxic gases and air quality [1, 2]. Typical atmospheric pollutants or toxic gases include nitrogen dioxide (NO_2), ammonia (NH_3), methane (CH_4), volatile organic compounds (VOCs), hydrogen sulphide (H_2S), sulphur dioxide (SO_2), and nitrogen monoxide (NO). These contaminants have detrimental impacts on the environment and people's health when exposure levels go above the advised limits [3]. However, the modern science and researchers have focused on developing or designing more feasible, durable, comfortable, and affordable gas sensors as well as continuously improving their properties. An ideal gas sensors or typical sensors should have as required silent features which include stability, selectivity, response, and constant speed recovery, etc. Such type of requirements are studied and improved using ideal gas sensors *via* nanotechnology [1, 4].

Nowadays, Nanotechnology has been providing a new dimension of modern research as well as providing fruitful ideas of modern solutions to any critical problem. This technology, basically reduces any dimensional size in nano-scale (below 100 nm) from the material's bulk state and is referred as nanomaterials. This size reduction incorporates unique optoelectronic and electrochemical properties. Therefore, Nanomaterials have been widely used in various applications such as LED, solar cell, and batteries, biomedical, hydrogen evolution, etc. [5]. Furthermore, significant advanced nanomaterials such as conducting polymers, metal oxide, chalcogenides, carbon nanostructure, and two-dimensional materials have been frequently used as gas sensor applications as the recent increase in published research indicates [1]. Figure 1 represents the research works done in the past decade on metal oxide-based NO_2 gas sensors. There is large number of active sites on surface of metal oxide, which is helpful in the gas sensing operation. Further, these properties can be associated to the amount of crystallinity, particle size, and the number of defects in its structure. There have been studies done on the different structures such as nanorods, nanoparticles, nanoflowers for the application in NO_2 gas sensors. These have been studied for their sensitivity, toxicity, cost-effectiveness, chemical and thermal stability. Not only this, but there are numerous materials such as polymers, Carbon Nanotubes, 2D materials like MoS_2, Oxide Nanoparticles, TMDs, Graphene, etc. which have been researched and studied for NO_2 sensing.

The overall number of papers that have been published in this domain is given in Fig. 1, which clearly shows that such studies have been increasing each year. However, traditionally operating range of metal oxide gas sensors is about 100–400 °C. Resulting in the use of high power which further decreases the sensor's stability and service life. This happens because there is grain growth of the metal oxide [1, 6]. Gas sensors based on conducting polymer can function at ambient temperature, still, humidity can cause them to degrade, resulting in slow response, long recovery times, and poor stability. Carbon nanostructure (nanotube) gas sensors have a slow reaction and recovery time due to the nature of this material for gas

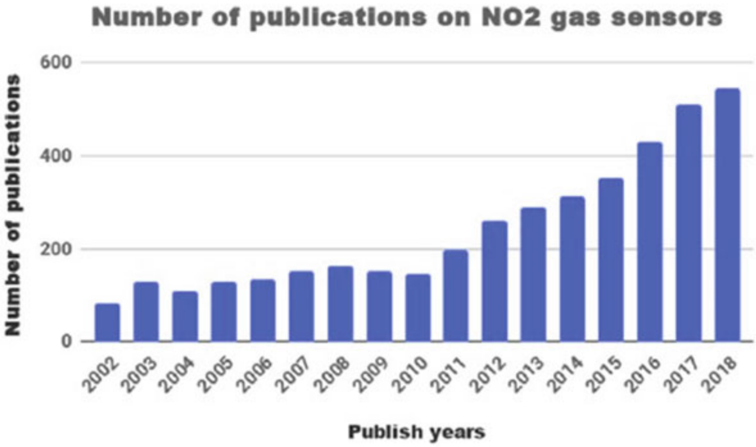

Fig. 1 The number of publication on NO_2 gas sensors from 2002 to 2018 (internet search of the web of science). Keywords for search: NO_2 gas sensor

adsorption and desorption process [1, 7]. Chalcogenide alloy-based gas sensors show high sensitivity, quick response in the ppm concentration range, and operate at room temperature [8]. But few sensors that are based on metal sulfide can operate at ambient temperature and also use low power [3]. Although two-dimensional metal dichalcogenides have been useful for gas sensing, but recovery has been poor. Use of thermal aid or UV light has been observed to improve recovery, but also increasing the energy consumption [9, 10]. Therefore, there are some limitations of metal dichalcogenides but its performance parameters such as sensitivity, recovery, etc., can be improved, *via* functionalization groups, dopants, and metal oxides [1].

In this chapter, we are discussing gas sensors based on chalcogenide semiconductor which is operated at room temperature. Chalcogenide-based gas sensors are a novel class of gas sensors that are being proposed to track air pollutants in an ambient environment.

Chalcogenides semiconductors are also recognized as solid-state materials which are made up of chalcogen from sixth group of periodic tables, some of these are Te, Se, S, etc. [11]. Chalcogen has a valence shell consisting of two s-state and four p-state valence shells. These substances, which are categorized as semiconductors, can be either crystalline or glassy (amorphous). Chalcogenides combined with one or more elements (metal or transition metals) like As, Ge, Si, Pb, Sb, Bi Cd, In, Zn, etc., enable to be formed in a broad number of binary, triply, and ternary systems such as artificial dimorphite (Al_4S_3), Tellurium alloys, PbS, CdS, ZnS, etc. The peculiarities of chalcogenides materials are caused by the chalcogen atoms' distinctive electronic structure, which is comprised of lone-pair electrons as well as without rupturing any chemical bonds with the valence, these electrons can be released or even become free. The chalcogen atom seems to be two coordinated, or bivalent, in the chalcogenide's alloys. The peculiar chemistry of chalcogenides semiconductors and defect states known as VAP (Valence alteration pair) that can capture and release the entities carrying charge, and act as charge acceptor and donor, which gives rise to the unique properties of these materials.

Chalcogenides are used extensively in the microelectronics and opto-electronics field, including in imaging devices, photo-thermal recording devices, gas sensors or chemical sensors, etc. [11]. Furthermore, most familiar chalcogenides-based alloy materials such as artificial Dimorphite (Al_4S_3) and Tellurium alloys have been utilized in gas sensors for specific detection of propyl amine and NO_2 (or NH_3) gas, respectively [8]. Similarly, Metal chalcogenide such as CdS based gas sensor has been frequently used for detection of SO_2 and NH_3 [12]. However, modern sciences have been exploring chalcogenides with transition metal referred to as two-dimensional (2D) transition metal dichalcogenides (TMDs) materials and invested in their various properties and fruitful applications.

TMDs are those substances having, MX_2 as its chemical formula where X is chalcogen such as S, Se or Te, and M is a transition metal like Mo, Nb, Hf, Zr, V, Re, or W. [1, 12, 13]. Many researchers have become interested in two-dimensional (2D) materials due to their exceptional and varied electrical, mechanical, and optical capabilities. We can accommodate in particular the semiconducting TMDs, which are of great interest, because they have a significant band gap between 1.5 and 1.9 eV [14, 15]. These materials' band gaps change from indirect in bulk to direct in the monolayer state. Additionally, various factors including their thermal stability, high surface-to-volume ratio, and capacity for producing affordable devices have led to their usage in optoelectronics, electronics, and as gas sensors [16]. The detection of gaseous molecules is done using semiconducting gas sensors [17]. These sensors' operating principles are typically dependent on how the electronic structure of the sensor material (such as conductivity) changes as a result of the adsorption of the gas molecules.

Monolayer TMDs' optical, electrical, and mechanical characteristics have been the subject of numerous theoretical investigations, [18] but their potential as gas sensors has received less attention. In recent studies, Ko et al. studied that, how acetone and NO_2 exposure affected the current of pristine WS_2 gas sensors. Additionally, they enhanced the 2D WS_2 nanosheets' capacities for gas sensing. 2D TMDs were discussed as a sensor material for chemi-resistive gas sensors in these studies. The optical and electrical sensing capabilities of semiconductor TMDs as gas sensors are predicted using a first-principles calculation based on density functional theory (DFT) when exposed to NO_2, NO, O_2, and NH_3 gas molecules. Before exposure and after exposure to these four gas molecules under study, the transfer characteristics and dielectric function were computed. The understanding of how semiconductor TMDs react to gas molecules can be a valuable resource for the creation of gas sensors [19].

There are many different operating principles for gas sensors, including those that use optical absorption, reflection, or fluorescence, thermal, sound propagation, or electrical conductivity, etc. Different types of gas sensors are indicated in Table 1. The receptor and transducer are two crucial parts of a gas sensor. The transducer further transforms the chemical interaction between the receptor and the target

Table 1 Various types of gas sensors with different working principles

S. no.	Sensor type	Physical change measured
1	Optical sensors (thin film or fiber optic)	Optical path length, fluorescence, Reflection, absorption interferometry, or refractive index
2	Electrochemical gas sensors (such as amperometric gas or potentiometric amperometric gas sensors)	Electrical current or change in electromotive force
3	Field effect gas sensors: diodes, transistors	Change in the work function
4	Piezoelectric gas sensors (such as microcantilevers, quartz crystal microbalances, surface acoustic wave)	Change in mass
5	Chemiresistive sensors	Electrical conductivity/resistivity
6	Capacitive sensors	Change in capacitance

analyte molecule into an analytical signal. In gas sensing, a variety of transduction strategies are possible depending on the changes either physical or chemical that are being detected [20]. We will briefly discuss of various operating principles used for gas sensors in the below session.

Let us take an example to understand the gas sensor through a schematic diagram Fig. 2. We will look at the optical gas sensor which was prepared by Ashkavand et al. (Developed Low Temperature Anionic 2H-MoS_2/Au Sensing Layer Coated Optical Fiber Gas Sensor).

The preparation of gas sensor fabrication starts from the synthesis of the MoS_2 using various precursors *via* hydrothermal method which helped to obtain the crystalline MoS_2 particles. Fabrication of sensor was initiated by firstly preparing the sensing layer, for which optical fiber was grinded to remove the cladding of multimode polymer optical fiber. The uncladded portion was polished and then coated with a layer of thin film of MoS_2. And Au film was deposited using Magnetron sputtering for realization of robust and homogenous layer of MoS_2. After fabrication it was then tested for transmission for which Transmitted Light intensity modulation principle was used, which is an evanescent wave intrinsic sensor, to monitor the optical spectrum. White light was also used to monitor the changes in light intensity and output. Sensor was then put inside chamber of stainless steel filled with organic vapors to detect the N_2 gas as depicted in Fig. 2b [21].

2 Synthesis Method of Chalcogenides

The alloys of chalcogenide are synthesized generally by using pure elements and melt-quenched [11]. Metal sulfide is synthesized by methods such as chemical precipitation [22], hydrothermal or solvothermal, etc., [3] while 2D transition

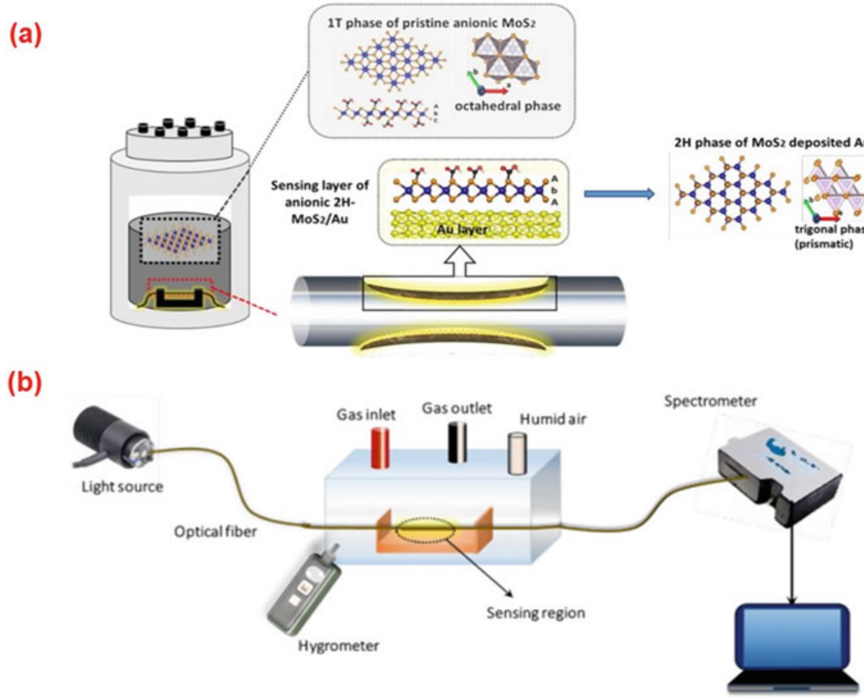

Fig. 2 **a** Diagram showing the preparation of pristine anionic 1T-MoS_2 and the surface functionalization of Optical fiber with coating sensing layer, i.e., anionic 2H-phase MoS_2/ Au, using recovery hydrothermal method. **b** Diagram showing the gas sensing mechanism including the gas sensing transmittance setup using the as-prepared sensor from [21]. Copyright (2020) American Chemical Society

metal dichalcogenides are synthesized including liquid exfoliation, micromechanical exfoliation, and CVD, etc. [1, 23, 24].

There are of few examples of synthesis or fabrications of chalcogenide-based materials given below in Table 2.

2.1 *Performance Parameter of Ideal Gas Sensors*

Ideal gas sensors are expected to be highly sensitive and selective, quick reaction and recovery times, stability for long duration, and very less power consumption. These are the typical requirements for an efficient gas sensor. Here, a set of characteristics, such as responsiveness, selectivity, sensitivity, dynamic range, LOD, response and recovery time, and stability, are specified to assess and differentiate for improving the performance of various sensors.

Table 2 List of various synthesis or fabrication methods of chalcogenide-based materials for gas sensors

S. no.	Category	Chalcogenide-based gas sensor	Synthesis methods/ fabrication methods	References
1	Chalcogenides alloys semiconductor	Artificial dimorphite (As_4S_3)	Melt quenching	[11, 37]
		Tellurium alloy (As-Ge-Te)		
2a	Metal sulfide nanomaterials	SnS	PVD	[25]
2b		ZnS	Hydrothermal	[26]
2c		PbS	Chemical deposition	[27]
2d		CuS	Deposition	[28]
2e		CdS	Sol–gel	[29]
3a	2D-transition Metal dichalcogenides	MoS_2	CVD	[30]
3b		MoS_2-RGO	Wet chemical	[31]
3c		RGO-MoS_2-CdS	Solvothermal	[32]
3d		MoS_2/PSi NWs	Chemical etching + CVD	[33]
3e		WS_2	CVD, ME	[34]
3f		WS_2@CTCFNs	Electrospinning	[35]
3g		WS_2/GA	Aerogel conductometric	[36]

2.1.1 Response

For a given gas concentration unit, response of gas sensor is defined as, variation that occurs in the capacitance (C), current (I), resistance (R), light power (P), effective refractive index (RI), conductance (G = I/V), and resonant frequency (f) with respect to the signal in the absence of analyte molecules, that takes place during operation. It's described as follows:

$$\left(X_{\text{gas}} - X_0\right)/X_0 = \Delta X/X_0 \tag{1}$$

Here, X is one of the following: C, I, R, P, RI, G, and f, X_{gas} is the signal of sensors following the adsorption of analyte gas, and X_0 is the baseline signal (no analyte gas). The analyte gas may cause various reactions at various concentrations. The modification of the testing signal is presented in this evaluation using response in percentage or response $\% \times$ response $= 100\%$.

2.1.2 Sensitivity

The ability to distinguish between little variations in an analyte's mass or concentration is referred to as sensitivity. In other words, in the calibration graph, its slope depicts the variance in the sensor's response for a unit concentration of gas and it represents the sensitivity of the sensor. Therefore, Sensitivity (S) is equal to response/concentration. Hence, the efficiency of the sensor is its higher sensitivity.

2.1.3 Selectivity

The term "selectivity" describes a target gas's strong adsorption in a mixture of gases still being not sensitive toward other gases of the mixture. The following formula represents the selectivity factor/coefficient (K) of the "target gas" to another gas:

$$K = S_1/S_2 \tag{2}$$

Here, S_1 and S_2 represent the sensitivity of sensor toward target gas and a different gas, respectively.

LOD is an indication of the minimal concentration of a detectable analyte used in chemical sensing. As per the International Union of Pure and Applied Chemistry (IUPAC), formulations of LOD have traditionally been based on the use of linear regression models. The theoretical LOD can be determined from the slope of the linear section of the response curve, or "Sensitivity (S)," and the Root-Mean-Square (RMS) variation at the baseline, when the signal is three times stronger than the noise.

$$\text{LOD} = 3 \times \text{RMS}_{\text{noise}}/S \tag{3}$$

$\text{RMS}_{\text{noise}}$ is the noise level when there is no analyte gas present. Burgu'es et al. developed a method to estimate LOD by linearized calibration models with regard to the LOD in a non-linear gas sensor, such as metal oxide sensors, gas FETs, or thermoelectric sensors. The temperature at which a sensor is most sensitive is known as the operating temperature (OT).

2.1.4 Response Time and Recovery Time

Time duration needed to achieve at least 90% of the response and time duration needed so that 90% restoration occurs in the device's original value are referred to as the response time (τ_s) and the recovery time (τ_r) respectively. They are primarily employed as a measure of response time, which is greatly influenced by the kind of gas, device design, and exposure duration. A sensor's stability is determined by its capacity to deliver reliable findings over an extended period.

Whenever sensors are exposed to dangerous, corrosive, or hot environments, this statistic becomes crucial. A typical ideal gas sensor would have fast recovery and low reaction times, low LOD, high sensitivity, selectivity, and stability. However, the requirements of the designated environment or working circumstances will determine how it will be used in the end. Additionally, the sensor materials, substrate, environmental conditions (temperature, humidity, and pressure), as well as the testing arrangement, could all have an impact on the parameters (volume, shape, and gas flow rate).

3 Classification of Chalcogenides-Based Gas Sensor

For the understanding, we can categorize chalcogenides on the basis of combination with either by metal or transition metals.

3.1 Metal Chalcogenides Gas Sensor

Chalcogenides are combined with metal such as As, Ge, Si, Pb, Sb, Bi, etc., to form binary, triply, and ternary systems such as artificial dimorphite (As_4S_3), Tellurium alloys, PbS, etc.

3.2 Transition Metal Chalcogenides Gas Sensor

Chalcogenides are combined with transition metal either in mono form or di form. The mono form is formulated by MX whereas di form is represented by MX_2. Where M stands for transition metal ions and X stands for chalcogen. For MX included CdS, CuS, CdSe, etc. while MX_2 such as 2D-WS_2, 2D-MoS_2, etc. Some of the chalcogenide-based gas sensors are discussed below for a better understanding.

3.2.1 Tellurium Alloys

Tellurium alloys are excellent chalcogenide materials for the creation of gas sensors due to their adaptable structure and wide range of characteristics. Although numerous gases can be detected using sensors made of these materials, nitrogen dioxide, one of the most hazardous gases emitted by combustion, plants, and automobiles, was shown to have the maximum sensitivity (i.e., selectivity).

Figure 3a shows the surface morphology of Te film in a polycrystalline layer having ~1.0 mm–sized grains, i.e., textured in plane substrate. Figure 3b displays characteristics I–V plot of Te films carried out in NO_2 vapor and air. The linear dependence adheres to Ohm's law. The layer resistance reduces irrespective of the bias voltage's direction when NO_2 vapor is present, increasing the current. The electrical conductivity of the sensitive layer, or the slope of the I/U characteristics, rises when gas concentrations increase. The conductivity of the layer in relation to the gas concentration is shown in the inset of Fig. 3b. When the NO_2 mixture is turned off, both the conductivity and the I versus U curves return to their initial positions. Figure 3c shows the sensor sensitivity as a function of NO_2 gas concentration. At lower gas concentrations, it exhibits high sensitivity. Consequently, these sensors can monitor the environment for NO_2 up to 3 ppm. These observations are further supported by the transitory features (Fig. 3d). Figure 3d depicts the current flowing through a sample as the NO_2 gas mixture is repeatedly turned on and off while maintaining a constant bias voltage. The switching schedule appears as a dotted line. NO_2 vapor was applied in the following concentration steps: 0, 0.75, and 1.5 ppm. The current runs accordingly to schedule, however for adsorption and desorption processes, the saturation time is much different. Although the recovery time is longer than the reaction time, there is little drift in the baseline. The gas-induced current does not appear to be Drifting et al. [37].

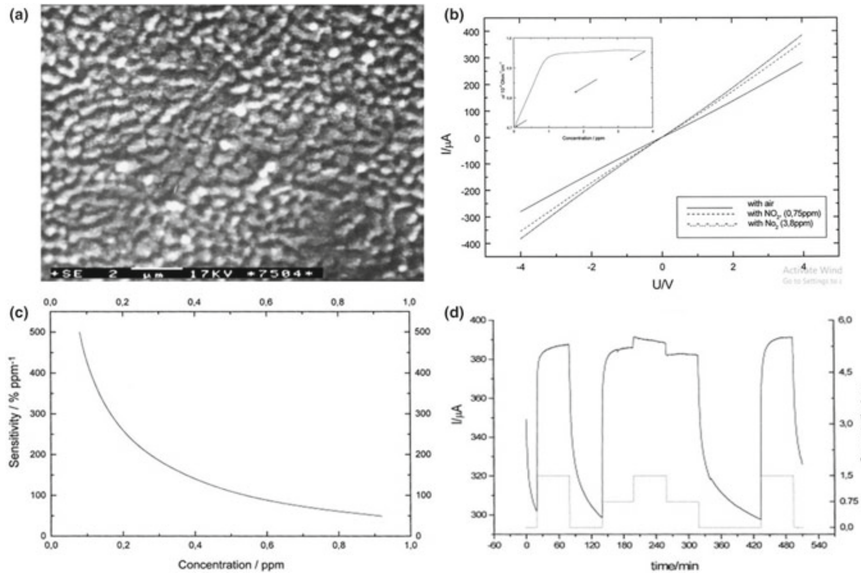

Fig. 3 **a** Shows scanning electron microscopy (SEM) of the highly sensitive surface tellurium (Te) film, **b** current (I)—voltage (V) characteristics of Te thin films in NO_2 vapor and air (*inset*: the conductivity against gas concentration), **c** gas concentration against sensor sensitivity to NO_2 at ambient temperature, **d** the tellurium-based gas sensor's transient behavior toward pulses of NO_2 vapor at room temperature from [37]. Copyright (2001) Elsevier

3.2.2 CdS Nanomaterial-Based Gas Sensor

Herein, we briefly explain the response study with various toxic gases using a CdS-based gas sensor. The inorganic chemical with the formula CdS is called cadmium sulphide. With three phases, CdS features a wurtzite-type (W) crystal structure in bulk form with an a and c of 0.4160 and 0.6756 nm, a cubical zinc blend (Z) structure in nanocrystalline form and a high-pressure rock phase. CdS were synthesized by the chemical precipitation method. The semiconductor CdS nanoparticle-based sensors were created using spray technique. Figure 4A shows the surface of CdS films formed under various circumstances examined by SEM. These films are not homogeneous and contain both small and large grains, some of which resemble crystallites. Most of the particles size are in the range 1–26.2, 5.7–63.2, 11.3–83.8, and 14.4–105.1 nm respectively [Fig. 4A (a–d)] The particle size present in CdS films prepared at 335 K is less than that in CdS films prepared at ambient temperature. This indicates that CdS has more active adsorption centers and larger surface areas. In other words, sensors based on CdS produced at 353 K might react to the gas more effectively. Figure 4B (a) and (b) show response studies were performed with various inorganic including NH_3, NO_2, H_2S, SO_2, water vapor and CH_3COCH_3, CH_3OH, C_2H_5OH, HCHO, $CHCl_3$, C_7H_8, C_4H_8O and $C_4H_{10}O$, C_6H_6. It was observed that the sensors are sensitive toward NH_3, H_2O, and H_2S at room temperature but not the sensitivity with organic solvent, NO_2, and vapors water vapor. Sensor responses to SO_2, H_2S, and NH_3 are impacted by CdS preparation conditions. The greatest responses to SO_2 and NH_3 are 233.9 and 189.6, respectively, for the CdS-based sensor produced by using Na_2S at temperature of 353 K and working voltage of 5 V. The CdS sensor produced using H_2S at temperature of 353 K responds to H_2S to a maximum of 88.5 at an operating voltage of 10 V. CdS synthesized at 353 K had a larger impact on the SO_2 reaction than CdS prepared at ambient temperature, whether H_2S or Na_2S is used as the precipitating agent.

Furthermore, The CdS-based sensor gave linear response to NH_3 from 0.3 to 6.0% and to SO_2 from 0.5 to 1.7% when manufactured with Na_2S at 353 K. The CdS-based sensor gave linear response to NH_3 from 0.08 to 1.1% and to SO_2 from 0.25 to 1.5%, as well, when produced with H_2S at working temperature of 353 K. Each sensor's response time and recovery time were below 54 s and 70 s, respectively. The response of the sensor was strongly influenced by temperature and operating voltage. Figure 4C displays the sensor response transients to SO_2, H_2S, and NH_3 at 10 mm film thickness. Figure 4C (a) shows the recovery times and sensor's reaction to SO_2 are under 50 s and 15 s respectively. The recovery and response periods to H_2S are less than 70 s and 32 s respectively [Fig. 4C (b)]. Figure 4C (b) shows the CdS recovery time is quicker at 353 K. It may be due to a sensor operating at higher voltage exhibiting strong electrostatic repulsion. Consequently, enhances the desorption rate of gas molecules. The response and recovery periods to NH_3 are depicted in Fig. 4C (c) to be less than 65 s and 54 s, respectively. Based on these conclusions, the CdS-based sensor is capable of recognizing SO_2, H_2S, and NH_3 effectively [12].

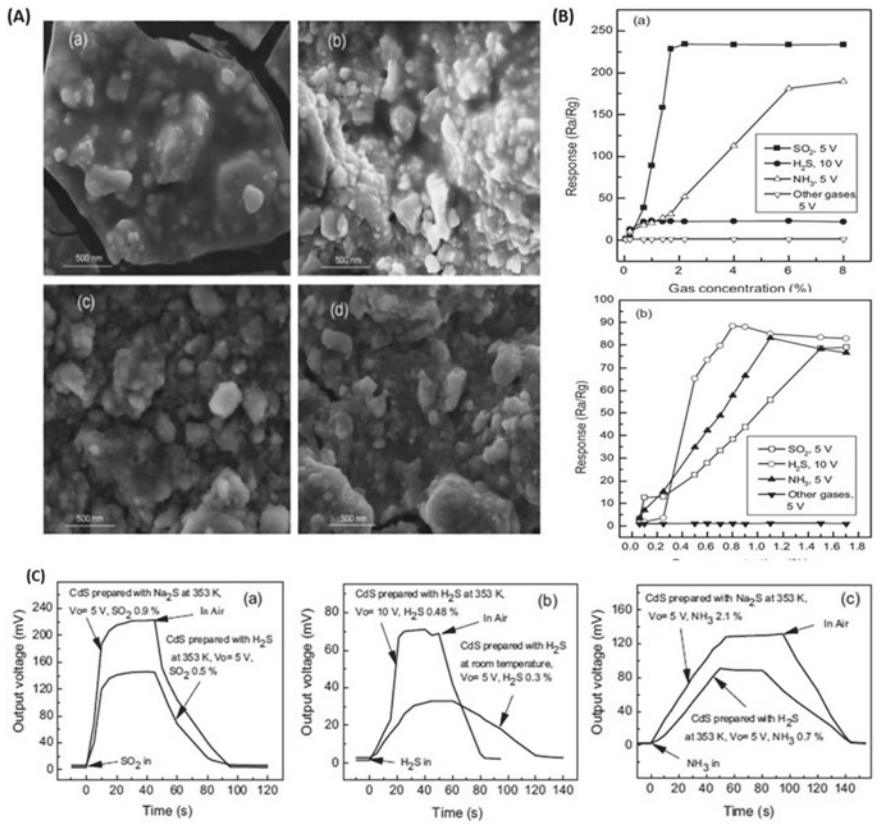

Fig. 4 **A** SEM view of CdS film: (a) preparation of CdS with Na_2S at 353 K, (b) preparation of CdS with H_2S at 353 K, (c) preparation of CdS with Na_2S at RT and (d) CdS prepared with H_2S at room temperature. **B** Two distinct CdS-based sensors' typical reactions to test gases when operated at optimal operating voltage and ambient temperature (a) At 353 K and, CdS and Na_2S were produced. (b) H_2S and CdS were produced at 353 K. **C** Response of transients CdS-based sensors for (a) SO_2, (b) H_2S, and (c) NH_3 from [12]. Copyright (2013) Elsevier

3.2.3 $MoSe_2$ Nanoflakes-Based Gas Sensor

Figure 5A (a) shows $MoSe_2$ micro-powder was exfoliated into nanoflakes utilizing a mixed solvent strategy and a well-known sonication-centrifugation process. These exfoliated $MoSe_2$ are FESEM pictures and low-magnification TEM images shown in Figs. 5A (b) and (c), respectively, which clearly demonstrate the nanostructure. In Fig. 5A (d), the SAED pattern is depicted as an inset HR-TEM picture of the exfoliated $MoSe_2$ nanoflakes to a plan-view. Figure 5A (e) displays height profile topographic and AFM image of exfoliated nanoflakes along with 2–3 thickness layer $MoSe_2$ nanoflakes (thickness of monolayer $MoSe_2$ is ~07 nm.) (Inset: $MoSe_2$ is depicted hexagonal symmetry in the atomic resolution image from SAED data). Two terminal devices' temperature-dependent current (I)–voltage (V) data were gathered at various temperatures and are displayed in Fig. 5B (a) 2 V to +2 V range. The device exhibits a typical ohmic characteristic between 50 and 200 °C. By exposing a sensor to H_2S gas at various temperatures, it was determined that the device response follows an "increase-maximum-decay" trend with the maximum at 200 °C temperature along with the best response and recovery times.

Figure 5B (b) shows how the sensor response changed when the H_2S concentration increased from 5.45 ppm to the operating temperature. As a result, this temperature has been used for all the gas sensing measurements. Figure 5B (c) displays the real-time current and dynamic transient response. The sensor was given time to recover in ambient, and a response in the range of 53.04 to 18.57% (with respect to 5.45 ppm to 50 ppb of H_2S gas) was obtained. Afterward, recovered in the artificial air environment, the same device's reaction is noticeably reduced.

According to Fig. 5B (d), response in the range of 19.8–7.13% (with respect to 5.45 ppm–500 ppb of H_2S) was attained. According to the results given in Fig. 5C (a), the sensor's reaction time and recovery time for a concentration of 100 ppb H_2S are 15 s and 43 s, respectively. One of the key difficulties is the repeatability of chemiresistive sensors. In order to assess this device was subjected to 1 ppm of H_2S

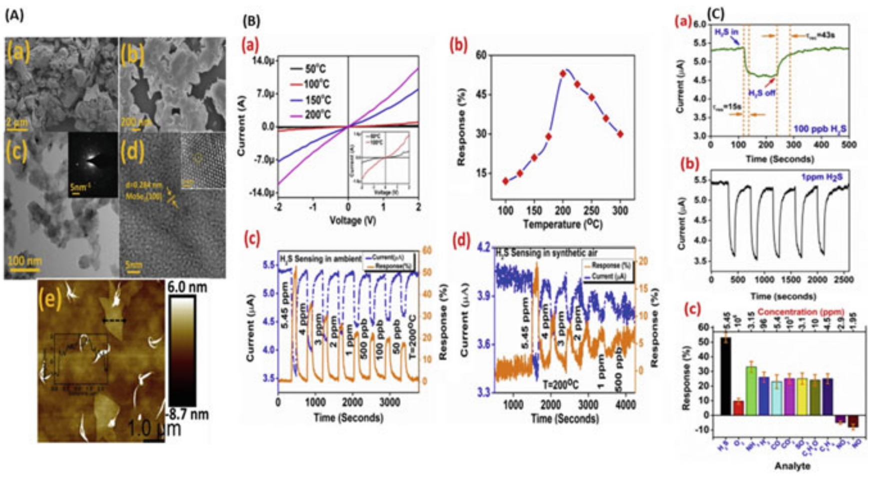

Fig. 5 **A** Field emission scanning electron microscopy (FESEM) image of (a) $MoSe_2$ (bulk) and (b) and $MoSe_2$ (exfoliated) (c) TEM image at low-magnification for exfoliated $MoSe_2$ (d) HR-TEM image of exfoliated $MoSe_2$ (e) atomic force microscope (AFM) height profile of exfoliated $MoSe_2$ nanoflakes. **B** (a) temperature ranges 50–200 °C for the current–voltage characteristics of sensing devices (b) Alteration of responsiveness with ambient environment temperature (c) Concentrations of H_2S from 50 ppb to 5.45 ppm in the ambient environment: dynamic sensing response and current variation at temperature 200 °C (d) Concentration of H_2S from 500 ppb to 5.45 ppm in synthetic air: dynamic sensing response and current variation at temperature 200 °C. **C** (a) Response and recovery times for a 100 ppb H_2S concentration in the ambient environment (b) 5 cycles of the sensor's repeatability while exposed to 1 ppm of H_2S gas (c) cross-sensitivity histogram with other reducing and oxidizing gases from [38]. Copyright (2019) Elsevier

for 5 continuous cycles (a cycle being defined as H_2S gas on and off for 120 s and 300 s respectively), and the signature of current is displayed in Fig. 5C (b). The current measurements for each of the 5 cycles clearly mimic one another, demonstrating the device's remarkable repeatability.

The histogram of the device's cross-sensitivity to various oxidizing/reducing gases such as SO_2, H_2, CO, O_2, NH_3, NO_2, CO_2, NO, VOCs, C_2H_4, C_3H_6O is shown in Fig. 5C (c). It should be mentioned that the sensor did not respond or responded poorly to analytes other than H_2S at lower concentrations (<500 ppb). At larger concentrations of various interfering gases, such as H_2S and NH_3 selective sensing by the device is still difficult. Doping and functionalizing TMDs with metal nanoparticles are potential ways to accomplish this. Cho et al. found that a gas detecting device made of MoS_2 nanosheets a semiconducting TMD similar to $MoSe_2$ fabricated with gold nanoparticles had high selectivity for volatile organic compounds. WS_2 nanosheets coated with platinum quantum dots have been shown by Ouyang et al. to be extremely selective toward NH_3 gas, even at room temperature [38].

There are some brief details and comparison of chalcogenide-based sensors for the detection of various toxic gases operating at room temperature shown in Table 3.

3.2.4 2D Transition Metal Di-Chalcogenides-Based Gas Sensors

Materials having a formula of MX_2, in which X is chalcogen and M is a transition metal like Molybdenum, Tungsten, Hafnium, Titanium, Zirconium, Vanadium, Niobium and so on, are known as TMDs (S, Se or Te). Two-dimensional (2D) TMD structures have drawn the attention from researchers because of the great sensing abilities that they exhibit, and distinctive chemical and physical characteristics, including the semiconducting property, and large surface-to-volume ratio. MoS_2, WS_2, ReS_2, $MoSe_2$, WSe_2, and $ReSe_2$ are examples of these atomically thin-layered 2D layered materials that have the potential to be efficient sensing materials. They can be created using a number of methods, such as liquid exfoliation, micromechanical exfoliation, and CVD. Because it works well for large-scale electronics, optoelectronic, and gas-sensing devices, the latter is the most frequently used. Although the recovery of these 2D TMDs was subpar, they were suitable for room-temperature sensing. The use of thermal assistance or UV illumination resulted in high performance, but energy consumption was a problem [48].

4 Use of Chalcogenides in Gas Sensors

The increased use of chalcogenides-based gas sensors can be attributed to a few unique properties that make them the perfect choice for gas detection. Chalcogenides are solid-state minerals formed when chalcogenide elements of the sixth group of the periodic table combine. These substances are classified as covalent semiconductors. These chalcogenides can be crystalline or amorphous in nature.

Table 3 List of chalcogenides-based sensors detection for toxic gases at operating room temperature

S. no.	Category	Materials	Pollutant analyte	Concentration	Response (%) or sensitivity	LOD	τ_s/τ_r	References
1A	Chalcogenides alloys semiconductor	Artificial dimorphite (As_4S_3)	Propylamine	40 ppm	0.1	–	–	[11, 37]
1B		Tellurium alloy (As-Ge-Te)	NO_2	3 ppm	~100	–	2–3 min/30–40 min	
2A	Metal sulfide	CuS/CuO	H_2S	1.88%	313,900	–	75 s/67 s	[39]
2B		PbS QDs/TiO_2	NH_3	100 ppm	1649*	2	~10 s/~10 s	[40]
2C		SnS	NO_2	0.1	20	–	NA/5 s	[41]
2E		PbS NCs/rGO	CH_4	10 000	45	–	90 s/65 s	[42]
2F		CdSe/ZnS (optical)	CO_2	100 vol%	84*	–	–	[43]
3A	2D-transition Metal dichalcogenides	WS_2	NO_2	0.1 ppm	9.3	100 ppb	5 min/25 min	[44]
3B		Ni-doped MoS_2	SO_2	5 ppm	7.4	250 ppb	51 s/73 s	[45]
3C		MoS_2	NO	2 ppm	80	0.8 ppm		[46]
4D		ZnO/MoS_2	C_6H_6	20	30	0.1	8 s /6 s	[47]

Chalcogenides' amorphous structure allows for numerous combinations with various elements, including binary, triple, and ternary combinations. Furthermore, it is unimportant how the materials in chalcogenide are stoichiometric. When we look at the valence shells of these compounds, we find that each atom has six electrons. The electrons in the s orbital are antiparallel, which gives it a unique sensing ability.

5 Principle of Chalcogenide-Based Gas Sensors and Development

Although chalcogenide semiconductors can detect gases, the precise method by which they do so is unknown. The valence band's upper portion is made up of lone-pair electrons, which appear to be the source of gas sensing in these materials. However, the lack of experimental data makes it impossible to build an acceptable and complete model. If there are flaws in the crystallinity, such as unsaturation of chemical bonds, these flaws will interact with lone-pair electrons (dangling bonds) [8]. Their dangling bonds interact with a lone pair near to them and bonds and modify its environment. The p-type of conductivity also referred to as positive thermoelectric power, is produced as a result of this interaction by the formation of release holes and lattice defects. Deep acceptors below the gap's center or close to the top of the valence band are caused by lattice defects. This is likely the key to understanding how these materials might be used for gas sensing because the dangling bonds behave as a dopant for the semiconductors with lone pairs. In reality, the surface of the semiconductor has the highest concentration of dangling bonds and the region where the crystal's periodicity is broken. As a result of lone pairs of electrons interacting with them, the surface of the grains develops a hole-enriched zone. As a result, there is an upward bending of band edges of p chalcogenide close to the surface and in the areas inside the grain. The bonding energy is significantly greater than the energy of correlation for additional electrons deposited on the lone-pair orbital, resulting in an exothermic process. Another effect of the reaction is that each contact converts dangling bonds into a localized VAP C +3 and C 1 defect, releasing two holes. As a result, the hole-enriched region includes the surface, grain boundary, and intra-grain areas. As a result, metallic contacts in some alloys are typically injecting or ohmic. As an example, consider nitrogen dioxide adsorption. After nitrogen and oxygen form a covalent bond, a single unpaired electron remains on one of the atoms in the nitrogen dioxide molecule. The gas molecule functions as a dangling bond, it absorbs lone pair of electrons and forms a pair of electrons as it gets adsorbed on the surface of the chalcogenide semiconductor. Following by capturing a lone pair of electrons, and the electron moves from the upper region of the valence band to an acceptor (gas) level, resulting in the realization of an extra hole. Majority of density of carrier in the grain boundary and inside the regions of grain, increases as a result of nitrogen dioxide adsorption, increasing the conductivity of the film region. Other gas chemisorption, of course, implies a number of reactions at the surface, which can increase or decrease the density of majority carriers in the areas of grain boundary, and thus the film's conductivity. However, there is the existence of a different gas-detecting mechanism which is dependent on the number of electrons present in the gas molecule, or the type of attachment of gas molecule to the chalcogenide material's surface (physical or chemical attachment). If there are any unbonded electrons left of gas molecules then sometimes they strengthen the relationships with chalcogenides or prevent them from reacting with other gas molecules.

Chalcogens atoms, in contrast to other compounds, increase hole density in the regions of accumulation, and hence the sensor film's conductivity increases. The film's electric and sensing properties. Furthermore, the proper selection of contact geometries is critical in the design of a dependable chalcogenide-based gas sensor. These are some of the contact geometries. Although there has been no systematic investigation into the use of optimized contact geometries, it has been discovered that each contact geometry has specific advantages for detecting specific gases. To obtain the electrical signal correlated with gas concentrations, various operation modes may be used. The majority of these operation modes have yet to be investigated. Only conductive and field effect transistor (FET) chalcogenide-based gas sensors have been built and tested so far.

6 Fabrication of Chalcogenide-Based Gas Sensors

6.1 Synthesis Method of Chalcogenides

The melt-quenching method is commonly used to create chalcogenides alloys from pure elements [11] and chemical precipitation, is used to create metal sulphide [22], hydrothermal or solvothermal etc. [3], while 2D transition metal dichalcogenides are synthesized using various methods including liquid exfoliation, micromechanical exfoliation, and CVD, etc. [1, 23, 24].

6.2 Fabrication of Sensor

By using the melt-quenching technique, chalcogenide alloys are typically created from pure elements. The synthesis is carried out in quart ampoules evacuated to less than 105 Torr. During the synthesis, the ampoules are agitated and rotated around the longitudinal axis to achieve homogenization. According to composition, the melting point and synthesis time range from 200 to 1000 °C and 10 to 100 h, respectively. After the ampoules have been quenched in the air or on a refrigerator. Typically, gas-sensitive thin films are created through vacuum thermal evaporation of synthesized materials onto Pyrex glass, ceramic, or silicon substrates using a tantalum boat. Evaporation occurs at pressures less than 105 Torr. As the film's velocity increases, so does the area of deposition. The large (1018–1019 cm^3 eV) concentration of localized states in the gap present in the glassy state of the chalcogenide semiconductors leads to a very short (about 100) Debye screening length. The basic operating principle of a semiconductor gas sensor, on the other hand, is the control of the surface or/ and interface potential barrier by adsorbed radicals. As a result, only ultrathin layers can provide a gas sensor device, and issues related to technology and physical and chemical stability become critical. These issues can be solved by using crystalline chalcogenides. The sensitivity decreases as the annealing temperature rises, but only slightly. Sensor sensitivity increases dramatically as thickness decreases. A compact layer's behavior is typical [49].

7 Conclusion

These methods allow for more precise control on the material's structures which include grain sizes or the grain boundary, and may enable making of the porous structures that are good for use in gas sensors. Review of different studies revealed that there are three types of nanomaterials that are porous which makes them suitable for room-temperature gas sensing. Chalcogenides have been shown to be suitable for instantly sensing harmful gases as well as instantaneously monitoring gases in humidity. However, these materials have significant limitations, most of which are related to the selectivity of gases and stability of the material in extreme environment. Furthermore, the gas-sensing mechanism for chalcogenides is still poorly understood. These limitations, we believe, will be overcome in the near future through surface functionalization and the design of heterostructures utilizing a wide range of nanomaterials. Aside from the strategies discussed in the review, several other avenues are being pursued.

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Functional Materials for Biomedical and Environmental Sensing Application

Shivani Bharti

Abstract The development in the technology and industrialization offers better living standards but along with that it causes severe environmental pollution and induces various diseases to living organisms. Technological advancement in the materials synthesis and functionalization have produced significant progress in molecular imaging and sensing, targeted and controlled therapeutic, detection of disease at an early stage and sensing of hazardous pollutants in the environment. Surface functionalization has gained greatest significance and is now recognised as a vital technique for the development and design of innumerable devices and engineered systems for critical technical domains in biomedical, biotechnological, and environmental applications. The development of unique multifunctional targeted devices and functionalized materials for sensing, as well as cutting-edge monitoring sensors for anticipating molecular changes, has advanced the efficiency of operations while lowering costs. A key objective of scientists to incorporate the functional groups over material is to enhance their properties for sensing applications by improving their physiochemical properties like selectivity, sensitivity and stability. Till date there is demonstrable improvement in the production of functionalized materials and their applicability in various sensing devices. This chapter would be discussing the synthesis of different functional materials for their practical applications in the biomedical field as biosensor and sensing of environmental pollutants. This chapter emphasizes on the importance of surface functionalization of materials followed by the different strategies used for the functionalization.

Keywords Functionalization · Biosensors · Polymerization · Bonding · Surfactants

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1 Introduction

The fast development in the technology and high degree of growth in industrialization is providing comfortable living conditions to the people but along with that also enhancing the environmental pollution and diseases [1]. There are various conventional techniques available for the sensing of pollutants or bio analytes like liquid chromatography, gas chromatography, mass spectroscopy or flow injection analysis. But these techniques are more time consuming, need specialized operation protocols, has complex sample preparation, is of high cost, requires an expert operator, and thus there was a need to find alternative methods for sensing applications [2]. Nanomaterials resulted in better efficiency for environmental pollutant sensing or biosensing than conventional methods owing to their high surface to volume ratio, tunable optical and electronic properties, and their high surface reactivity as shown in Fig. 1 [3].

Nanotechnology holds forth the possibility of significant advancements in telecommunications, electronics, health, and even environmental remediation. Nanostructured materials have provided the enhancement in the evolution of sensing devices used in various applications in the field of medical or environmental pollutants sensing. By modifying the surface of synthesized nanostructures, the properties of the nanostructure can be tuned in a controlled manner and improve their biological properties and functionalities [4, 5]. Surface properties govern the behaviour, performance and efficiency of the material. Surface modification provide unique potential to control the surface interaction and response which are needed for a particular application. By tailoring the materials surface their usage in technological fields is potentially infinite [6]. Thus, surface functionalization is of great importance

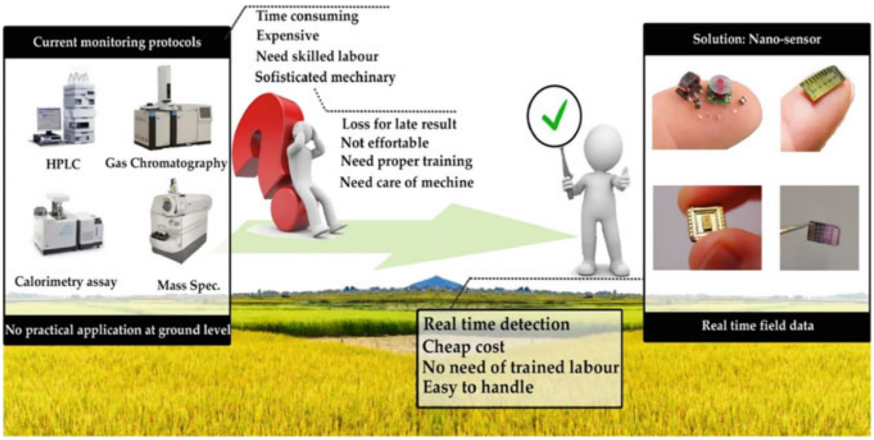

Fig. 1 Schematic representation showing the differences between traditional and advanced monitoring technologies. Adapted with permission from [11]. Copyright (2021) Springer

for developing and designing new materials as well as for prospective engineered systems.

As most of the biological molecules including membranes, protein complex, viruses consist of natural nanostructure, thus the nanomaterials have the potential to be adapted and used into biomedical devices. Anchoring of a specific functional group over the surface of the nanostructure widens the possibility of synthesizing different types of nanostructures for the removal of organic or inorganic pollutants from the environment and biosensing [7]. There are various methods adopted by the scientific community to modify and functionalize the surface of nanostructures using different reagents including chemical, physical or biological. With surface modification of nanomaterials many important properties are attained i.e., enhanced stability and solubility of nanoparticles in aqueous media, reduced cytotoxicity and new materials properties and functions [8].

The Scientific community has developed the synthesis strategies of nanomaterials to produce nanoparticles of different morphologies like quantum dots, nanotubes, nanosheets, nanowires etc. Functionalized nanomaterials and their nanocomposites are utilized for the sensing and removal of hazardous gases like SO_2, NOx, CO etc., toxic elements like As, Fe, Mn, nitrate, heavy metals, organic pollutants aromatic and aliphatic hydrocarbons [9, 10]. They are also used for the detection of biological substances like bacteria, viruses, antibiotics, parasites.

This chapter first describes the different categories of sensors based on the sensing mechanism or the type of analyte. The second section discusses various strategies utilized for the surface functionalization of the nanostructures for sensing applications. Further different categories of functionalized nanomaterials have been discussed which have been explored for biosensing and environment sensing.

2 Sensors

The word "sensor" originates from the Latin word "sentire" which basically means 'to identify' anything. Sensors mainly constitute of two elements i.e., receptor and a transducer as shown in Fig. 2. Receptor is an organic or inorganic substance that particularly interacts with a single analyte or collection of analytes, and in case of the biosensor, the biomolecule serves as the recognition component. The transducer, transforms chemical information into a quantifiable signal. A group of technologies that have been established over the last 15 years for the extremely precise and sensitive detection of environmental pollutants and biomolecules include nanomaterial enabled sensors. Biosensors works on the principal of capturing the biological signal and convert it into a detectable electrical signal [12]. The innovators Clark and Lyons began developing biosensors in the 1960s with the designing of glucose oxidase biosensor [13]. Enzyme-based, tissue-based, immunosensors, DNA-based, thermal, calorimetric, and piezoelectric, magnetic, are several types of nanosensors classified according to bioreceptors and transducers for sensing applications. Based on the sensing mechanism these sensors are characterized as field- effect transistor-

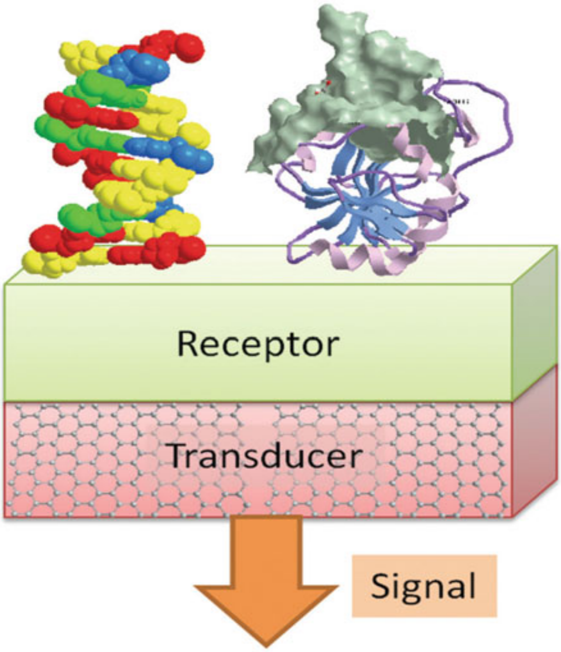

Fig. 2 Schematic illustration of a biosensor. The basic structure of biosensor constitutes of a receptor layer, which consists of a biomolecule (e.g., DNA or protein), and a transducer, which is a graphene-based material. Adapted with permission from [15]. Copyright (2011) Elsevier

based sensors, electrochemical biosensors, fluorescence, impedimetric biosensor, and surface plasmon resonance sensors.

In enzyme-based biosensors enzymes are immobilized over the device by using covalent bonding, van der Waals forces or ionic bonding strategy [14].

Polyphenol oxidase, oxidoreductases, amino oxidases, and peroxidases are some of the common enzymes used for the enzyme-based biosensors. In immunosensors antibodies are incorporated either of one type or multiple and are also referred as immunoassays. Despite various disadvantages i.e., pH and temperature sensitivity, short shelf life, high development cost in using antibodies, they are often used as the most selective recognition agent [16]. Nanobiosensors that use DNA primarily for recognition and nanomaterials for transducing purposes are called DNA nanosensors. Numerous DNA-based nanosensors have been developed for use by people in a variety of contexts, such as the detection of environmental toxins. The components of DNA like CA rich, T rich, mismatch DNA, ssDNA, C rich, dsDNA, aptamer, and G-quadruplex are explored for the detection of pollutants [17]. Using electrochemical sensing devices, the instrument can be brought to the sample site, which has a significant impact on the monitoring of various toxic pollutants (while traditionally the sample needs to be brought to the laboratory) [18].

Numerous studies highlighted the efficiency of biological sensors for monitoring significant environmental analytes in real-time. The classes of analytes that have been examined the most are pesticides, polychlorinated biphenyls, and heavy metals

[19]. Recent advancements in biosensors based on acute toxicity assessments in wastewater and sewage sludge were reported by Farre and Barcelo [20].

3 Functionalization Strategies

The key emphasis of nanotechnology is the development of nanostructures with controlled dispersion, tunable sizes, shapes, and chemical compositions with potential applications in human health and welfare. Numerous products and techniques using nanotechnology are available to improve environmental quality, minimise pollution, and preserve non-renewable and natural resources [21]. The surface reactivity of engineered nanostructures is very high, and leads to undesirable irreversible processes like aggregation due to instability. Also, bare nanoparticles show many challenges for their in vitro and in vivo use such as lack of biodegradability, poor biocompatibility, physiochemical instability, and acute toxicity [22, 23]. The particle reactivity is diminished due to the reduced specific surface area and interfacial free energy caused by aggregation. Thus, to optimize and improve the properties of engineered nanostructures to meet the demands of sensing applications on materials and adapt more nanostructure materials for biomedical and environmental sensing, the practice of modification of nanostructured materials is very essential. Functional nanomaterials can be synthesized using a variety of techniques which include CVD, hydrothermal, electrospinning, sol–gel method. The choice of technique depends on several factors, such as the desired properties, scalability, cost-effectiveness, and the level of control required over the size, shape and structure of the nanomaterial. Each technique has its advantages and disadvantages, and the selection of the appropriate technique requires a thorough understanding of the underlying chemistry and physics of the process.

The enhancement of engineered nanostructure stability is of paramount importance to chemists, especially for their prolonged utilization. Therefore, it is essential to develop various pathways such as using stabilising agents, doping and functionalization of nanostructure that are safe for the environment, non-toxic, and simple to implement. These strategies help to increase the lifespan of nanoparticles and prevent undesirable effects like aggregation in aqueous and organic medium, to avoid environmental contamination, as well as recycle and reuse nanoparticles. Doping affects sensing performance of a sensor depending on several factors, such as the type and concentration of the dopant, the type of sensing mechanism, and the target analyte. One of the main benefits of doping is the enhancement of sensitivity and selectivity of the sensor. In gas sensors, doping can increase the surface area of the nanomaterial, which can enhance the adsorption of gas molecules and improve the sensitivity of the sensor [24]. Doping also modifies the surface chemistry of the nanostructure, which can enhance the interaction between the sensor and the target analyte and reduce the response time of the sensor. But excessive doping can also lead to the formation of defects or impurities and reduce the sensitivity and stability of the sensor.

For biological applications encapsulation of such nanoparticles using biocompatible molecules such as biodegradable polymers and enzymes are offered as a greener approach to stabilize and functionalize nanostructures for their practical use. The functionalization and stabilization pathways should be biocompatible, i.e., non-immunogenic, nontoxic and hydrophilic stabilizing agents used for biomedical applications.

Functionalized nanostructures play a crucial role in improving the stability and durability of the sensor for biomedical and environmental sensing applications. The stability and durability of a sensor depends on its ability to maintain its sensing properties over time and under different environmental conditions, such as temperature, humidity, and chemical exposure [25]. Functionalization approach enhances the chemical stability, physical stability and improves the surface properties. Functional nanomaterials with high chemical stability can withstand exposure to a range of chemical compounds without losing their sensing properties. Functional nanostructures with high physical stability can maintain their structural integrity and sensing properties under different environmental conditions. In biomedical applications, functionalization of nanomaterials with biocompatible coatings improves their stability and reduces their potential toxicity. Therefore, by selecting the appropriate functional nanomaterial and optimizing their properties and structures, researchers design sensors with high sensitivity, selectivity, and stability for sensing applications.

3.1 Different Types of Interactions

There are five types of interactions possible between the adsorbent molecule and the synthesized core nanostructure surface which include hydrophobic interaction, hydrogen bonds, covalent, π–π bonds, electrostatic interaction. The type of interaction between both molecules affects their physical as well as chemical properties.

3.1.1 Hydrophobic Interaction

Hydrophobic interactions are mostly generated by proteins, enzymes or non-ionic polymers with nanomaterials [8]. They possess excellent adsorption properties because of the presence of hydrophobic segment in their structures. The hydrophobic end (the anchor block) of the copolymer adsorbed onto nanoparticles hydrophobic surface through hydrophobic interaction and hydrophilic block extends into the aqueous solution to form the hydrophilic layer [26].

3.1.2 Hydrogen Bonding

The bond formed when H atom is coupled with an element that has a high electronegativity in one molecule and an atom that has a high electronegativity in another molecule is commonly referred to as a hydrogen bond [27]. When the organic compounds or nanostructures have particular functional groups, such as –COOH, –OH, and $–NH_2$, hydrogen bonding interaction can develop and play a significant role in adsorption. In case of graphene sheets of Carbon nanoparticles, the benzene rings serve as the hydrogen-bonding acceptors, while the –COOH, –OH, and $–NH_2$ groups of organic compounds can act as hydrogen-bonding donors and establish hydrogen bonds with them [28].

3.1.3 Covalent Bonding

Covalent bonding occurs between the nanoparticle surface and material used for functionalization if both have certain functional groups such as $–NH_2$ –OH, and –COOH, [29]. The covalent bonding between the two can be analysed by various spectroscopic studies with XPS, FT-IR spectroscopy and NMR techniques. Typically, processes including carboxylation, amidation, diazonium, fluorination, free radical chemistry, bingel reaction, esterification, and composite creation are used for the covalent functionalization of nanostructures [30]. The covalent bond between the molecule used for functionalization and nanostructure is far stronger and can sustain any desorption as compared to noncovalent bonding interactions (such as hydrophobic, π-bonding, and hydrogen-bonding interactions) [31]. Thus, researchers widely use covalent modification of nanostructures to synthesize variety of nanostructures with excellent chemical and physical properties.

3.1.4 A π–π Bonding

π–π is another type of non-covalent interaction between the nanostructure and adsorbent. Spectroscopic techniques like Raman, NMR and fluorescence techniques are used to demonstrate π-π bonding interaction between engineered nanostructures and organic molecules. Through π–π stacking interactions, graphene has been widely employed to selectively enrich and detect aromatic compounds and single-stranded DNA (ssDNA) [32]. A π–π stacking between carbon nanotubes and proteins' aromatic residues (Trp, Phe, and Tyr) increases their adsorptivity and biocompatibility, making them less hazardous than pristine carbon nanotubes [33].

3.1.5 Electrostatic Interaction

If the charges on nanostructure and organic chemicals are opposite to one another, electrostatic attraction will result; otherwise, electrostatic repulsion will result.

Recently, the nanoshell of the polyelectrolyte on carbon nanotubes has been synthesized using a novel layer-by-layer electrostatic self-assembly method [34].

Functionalization of the nanostructure surface with an appropriate material, and a comprehensive characterization of physical, chemical and biological properties is most important. Parameters like timescale, pH, temperature and other environmental factors affect the surface functionality, reactivity, and overall performance of the material. Therefore, it is crucial to characterize the surface properties of the material using advanced techniques and study the influence of the above-mentioned parameters on the materials performance. Furthermore, to improve surface analysis and enable a quicker and more focused material development, breakthroughs in surface characterization techniques and trustworthy experimental methodologies are needed.

3.2 Different Types of Materials Used for Functionalization

For environmental or biosensing, nanostructures are mostly passivated with organic layers (surfactants or polymers like dextran, peg etc.), inorganic materials such as metals (e.g., gold, platinum), metal oxides (aluminium oxide, cobalt oxide), carbon, silica etc., to make synthesized nanostructure stable against oxidation, reduce aggregation, corrosion, increase physiochemical stability and solubility and provide functionalized surface [35]. Figure 3 illustrates the functionalization of core magnetic nanoparticles using polymer PEG. The functional coating/shell can be utilised for customising the biodistribution and immobilisation of foreign molecules in addition to improving its durability and suspensibility in biological environments as well as its biocompatibility [36]. This section discusses various types of materials used for the functionalization of different types of nanostructures.

3.2.1 Polymerization

The most common strategy followed by scientists to coat nanostructures is using polymers. The use of polymers over nanostructures prevents them from oxidation and provides stability [37]. Composites of nanomaterials of different shapes and morphologies (nanoparticles, wires, tubes, sheets, fibres, etc.) with polymers are used for environmental sensing of toxic gases and elements and for biosensing applications [38]. Nanocomposites of polymer and nanostructures are greatly explored by the researchers for the sensing and elimination of toxic gases (CO, SO_2, NOx etc.), [39] organic pollutants like aliphatic and aromatic hydrocarbons, hazardous chemicals (Manganese, Cadmium, lead, Arsenic etc.) and biological entities like virus, parasites, bacteria and antibodies.

Till now many polymers which are biocompatible, not toxic and environmentally safe have been explored for encapsulation purpose like polyethylene glycol, polyvinyl alcohol, poly(vinylpyrrolidone), chitosan, poly(lactic-co-glycolic acid)

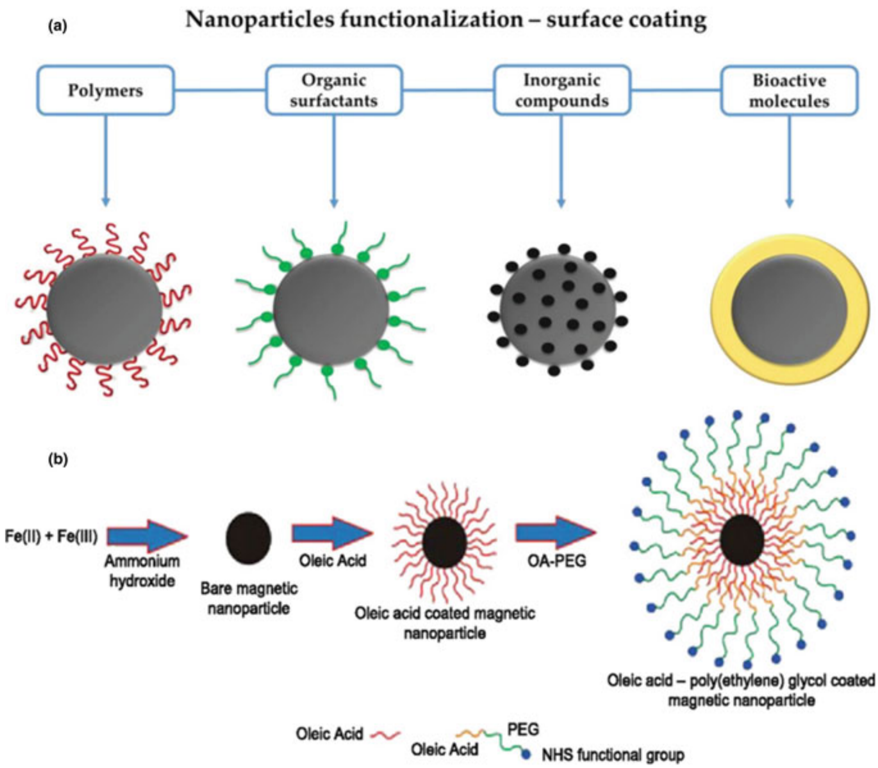

Fig. 3 Different strategies used for the functionalization of core magnetic nanoparticles surface. **a** Representing different type of materials used for iron-oxide core magnetic nanoparticles functionalization (IONPs). **b** Schematic for surface functionalization of magnetic nanoparticles with polyethylene glycol (PEG) [40]. Open Access (2022) Springer

etc. [41]. Polymers are widely used by researchers to functionalize various nanostructures like metals, metal oxides, graphene etc. to enhance the solubility in organic as well as inorganic solvents. The molecular weight of the polymer affects the size of synthesized nanostructure along with its morphology [42]. The surface area of the nanostructure can be grafted with higher coating density as polymers have multiple coordinating sites. Wide range of polymers with different molecular weights can be synthesized without losing their distinctive characteristic. The polymers can be used for ligand exchange also during the synthesis. According to Rozenberg and Tenne, nanoparticles which are stabilised by surface-active polymers, are not prone to aggregation because they are strongly adsorb onto the nanoparticle surface by van der Waals attractive forces between the surface and monomer units of the polymer chain, and their surface energy is significantly lower than that of pristine nanoparticles [43]. As the size of the nanostructures can be adjusted by controlling the length of the polymer chain and the modification of the surface of the nanosphere with appropriate functional group provides biocompatibility or ability to conjugate bioactive molecules. Thus, the usage of polymers for encapsulating phosphorescent dyes is mainly beneficial for bioimaging.

3.2.2 Surfactants

Surfactants are amphiphilic organic compounds, i.e., these molecules contains both hydrophobic (the tail) means water insoluble and hydrophilic (the head) means water soluble groups. Surface functionalization of the nanostructure can be done during the modification or after modification. Organic surfactants like oleic acid, mercaptoacetic acid, mercaptosuccinic acid, GSH etc. are some of the surfactants used for the stabilization and functionalization of nanostructures [44]. Surfactants can be classified as anionic, cationic, non-ionic, amphoteric. Organic functionalization of nanostructures helps the material to enhance the adsorption capacity, improve stability and bioavailability and also improves the drug release profile [45]. Additionally, the functional groups on nanoparticles can act as ligands to strongly bind to catalytic and organometallic complexes. Figure 4 shows that the functionalization of nanomaterials reduces the aggregation and enhances the stability and solubility of nanostructures in aqueous medium.

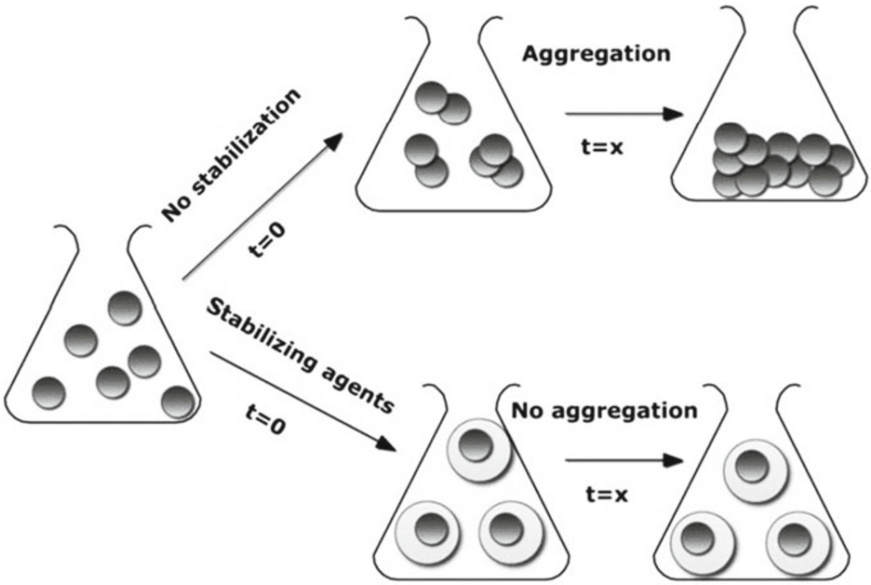

Fig. 4 Illustration of effect of surface functionalization on nanostructures aggregation in the presence and absence of functional groups. Adapted with permission from [46]. Copyright (2011) Royal Society of Chemistry

Ma et al. [47] synthesized rGO in the presence of three different surfactants i.e., sodium dodecyl benzene sulfonate (SDBS) (anionic surfactant); tetradecyl dimethyl betaine (zwitter ionic surfactant) and cetylpyridinium chloride (CPC) (cationic surfactant). They reported that the suspension of functionalized rGO in organic and aqueous medium changed significantly as compared to non-functionalized rGO. Yang et al. [48] synthesized L-cysteine functionalized graphene nanoparticles in aqueous medium for the detection of Cu^{2+} ions. The colour of graphene NPs changed from red to blue in the presence of Cu^{2+}. This colorimetric nanosensor with a sensitivity of 10^{-5} M, enables quick, and quantitative sensing of Cu^{2+}. Metal-doped nanoparticle preparation is typically done in aqueous-based medium by co-precipitating the cationic precursors and the doping element with the anionic reagent in the presence of the desired surface ligands. This will help in providing the necessary functional groups for additional bio-conjugation, such as thiol, polymers, phosphates, proteins, etc.

3.2.3 Inorganic

Depending on the application, the surface of the nanostructure can be modified with the inorganic molecule such as silica, metals, carbon, oxides (metal and non-metal) and sulfides. SiO_2 is most widely used as coating materials, since it enhances the dispersion of nanostructures in solutions, provides stability and protects against the acidic medium. Silanol groups offer various functional groups over the surface of the nanostructure and provide anchorage for ligands. Oxides and sulfides provide stability to the nanostructures without disturbing the magnetic properties. Fujihara et al. [49] have synthesized co-stabilized Au nanoparticles with fullerene-thiol and octanethiol. Marzan et al. [50] prepared SiO_2 functionalized citrate capped Au nanocomposites. Carbon is also explored as coating materials to help nanostructure's stabilization, prevents from oxidation, and is a low cost and high efficiency modification approach to enhance conductivity. Dopamine, glucose, aniline and other small organic molecules are some of the selectable sources of carbon.

3.2.4 Bioactive Molecules

Use of nanostructures in biomedical devices and systems have increased to a large extent owing to their unique and tunable properties. But there are also some limitations associated with nanostructures for their use in biomedical applications like non-specific targeting, cytotoxicity, biocompatibility and bioavailability [51]. To address these shortcomings the surface of the nanostructures is passivated with biological entity like bacteria, biomolecules, peptides, proteins, viruses, carbohydrates and cells known as biological functionalization. By using this approach, the physiochemical properties and functionalities of both the biological entity and inorganic nanostructure are brought together to form the hybrid material also referred to biohybrid or bio doped materials. Biomolecules can be immobilized over the nanostructure surface by using the physical, covalent or bio-affinity approach depending on the factors including surface properties of the material, nature of the biomolecule and application. After immobilization over the materials' surface the stability and properties of biomolecule may be lost due to the nature of biomolecule, surface properties and surface environment. Ren et al. [52] reported the facet selective binding of DNA to the surface of UCNPs. They found the strongest affinity of the phosphate group on the end of DNA to replace the hydrophobic surfactant molecules and createsa hydrophilic surface. Wang et al. [53] developed a sensitive electrochemical immunosensor based on single-walled carbon nanohorns functionalized with horseradish peroxidase-labelled MC-LR antibodies for the sensing of MC-LR toxins in Tai Lake water. The results showed that under optimal conditions, the immunosensors exhibit linear response varying from 0.05 to 20 mg/L with a detection limit of 0.03 mg/L. Nanoparticles based electrochemical sensors provide a platform for the detection of numerous toxins and monitoring of hazardous components in environment. Till now various nanoparticle based fluorescent biosensors and chemosensors are fabricated with sensing mechanism based on quenching or enhancement in fluorescence emission, energy or electron processes [54].

4 Functionalized Nanomaterials for Sensing Applications: Biosensing and Environmental Sensing

Practices adopted by humans for industrial development caused the soil, air, and water resources to significantly deteriorate. As a result, the levels of pollution in agricultural environments have substantially increased, having a significant negative impact on human and animal health. Various conventional techniques have been adopted for monitoring ecosystems like HPLC, mass spectroscopy, which can directly detect and quantify environmental contaminants. The development of these techniques is limited due to their high cost and maintenance, more time consumption and need of sophisticated appliances along with skilled personnel. Thus, to meet the need for simple, efficient and cost-effective methods, nanoparticles-based sensors have been developed.

High reactivity and large specific surface areas of nanomaterials make them excellent adsorbents, catalysts, and sensors [55]. Pollutants in the air and water can be degraded and scavenged using their unique properties. By using a mild centrifugal force or magnetic force (in the case of magnetic nanoparticles), the contaminants that have been adsorbed onto the nanomaterials can be removed. Several natural and engineered nanostructures have been explored for biosensing and environmental sensing applications including magnetic nanoparticles, metal oxides, II–VI, graphene, up conversion nanoparticles etc. There are various functional nanostructures explored by the scientific community for sensing devices, including nanoparticles, nanowires, nanotubes and nanosheets. For sensing devices, nanoparticles offer high surface area to volume ratio, easily functionalized, which enhances the adsorption of target analytes and improves the sensitivity of the sensor. Examples of nanoparticles used in sensing devices include metal nanoparticles (e.g., gold, silver, and platinum), metal oxide nanoparticles (e.g., titanium dioxide and zinc oxide), and carbon-based nanoparticles (e.g., graphene and carbon nanotubes). Nanowires and nanotubes provide a large aspect ratio and a high surface area-to-volume ratio, which enhances the sensitivity of the sensor and enables the detection of low concentrations of target analytes. Nanosheets are two-dimensional structures with a high surface area, which can enable the adsorption of target analytes and improve the sensitivity of the sensor. Nanosheets can also be functionalized with different functional groups or coatings to improve the selectivity of the sensor. Examples of nanosheets used in sensing devices include graphene oxide and molybdenum disulfide nanosheets.

The following section discusses various types of functionalized nanostructures of different categories explored for the sensing applications.

4.1 Metal Oxides

Metal oxides exhibit metallic, insulating and semiconducting characteristics and consists of positive ions of metal and negative ions of oxygen e.g., ZnO CuO, Tungsten oxide, titanium oxide, tin dioxide, Vanadium oxide. These materials possess intriguing properties including high optical transparency, wide band gap, mechanical stress tolerance, superconductivity, high carrier mobilities and high dielectric constant [56]. Metal oxides have attracted the attention of researchers as they are non-toxic, low cost and earth abundant and can be prepared using low-cost wet chemical methods. In the current scenario, the treatment of pollutants in air and water are of great important for protecting the environment. Since metal oxide materials offer improved electron transfer kinetics and high adsorption abilities, they have been included into new biosensing devices. The biomolecules must physically adsorb or chemically bind to the metal oxide materials in order for the biosensing process to work. The ability of a biomolecule to effectively interact with metal oxide materials assures a higher rate of electron transfer and helps the biomolecule sustain a steady biological activity. It has been demonstrated that the positive charge and hydrophobicity of the metal oxides, when added to unlike surfaces, can enhance the attachment of negatively charged bacteria [57]. For the fabrication of high-performance biosensing devices, this property is especially crucial.

Two types of semiconducting metal oxide sensors i.e., n-type (ZnO, V_2O_5, W_2O_3, TiO_2 etc.) and p-type (CuO, SnO_2) has been explored for sensing applications. Environmental scientists and engineers are frequently interested in learning whether a particular contamination is present at a field site and whether its concentration is above the legal limit, in which case a device for the detection of such particular contaminants needs to be created.

WO_3 hybrid nanorods were functionalized with Platinum nanoparticles for the sensing of methanol and ethanol sensing [59]. At 220 °C by varying the concentration of ethanol and methanol (1, 5, 20, 100 and 200 ppm), it has been concluded

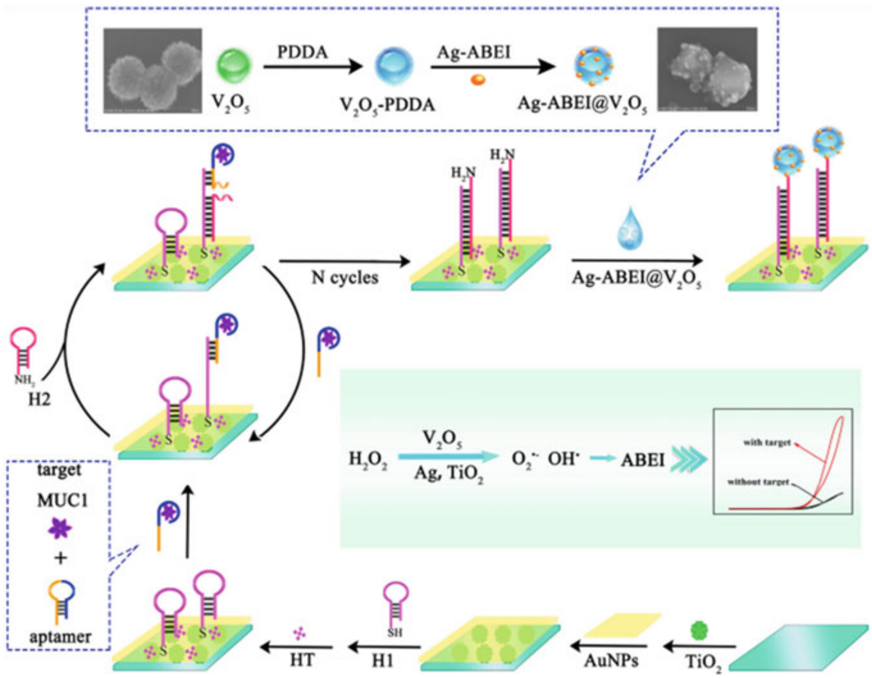

Fig. 5 Preparation of the ECL aptasensor and mechanism of sensitive detection of MUC1. Adapted with permission from [58]. Copyright (2018) Elsevier

that functionalized WO_3 nanorods show better performance than pure WO_3. Yang et al. [58] fabricated V_2O_5 based electrochemiluminescence added to ABEI (*N*-(4-aminobuthyl)-*N*-(ethylisoluminol) and functionalized with Ag nanoparticles for the sensing of mucin (biomarker related with pancreatic and breast cancer). Yang reported that loading of luminophores is increased due to the presence of V_2O_5 nanospheres and electrochemiluminescence signal is also enhanced shown in Fig. 5.

4.2 *Magnetic Nanoparticles*

Magnetic nanoparticles have attracted tremendous attention in solving the environmental problems and advancement in the biomedical applications. The remarkable properties of magnetic nanoparticles like super para magnetism, size, biocompatibility, ease of functionalization and physiochemical stability have benefited the medial and environmental fields including biosensing, tissue repair, cell separation and detection, magnetic hyperthermia and sensing of heavy metals [60]. Magnetic nanoparticles are generally consisting of elements like cobalt, nickel, iron and their oxides such as magnetite (Fe_3O_4), nickel ferrite, maghemite (Fe_2O_3), cobalt ferrite etc. Magnetic nanoparticles are usually physiochemical stable, environmentally safe and biocompatible, thus providing unique characteristics for sensing applications. Magnetic nanoparticles are usually coated with inorganic materials like metal oxides, silica, metals etc. and organic layers like surfactants or polymers which stabilise them against oxidation, corrosion and aggregation, enhances their physio-chemical stability and provide a functionalized surface. Parameters like size, morphology, presence of defects, doping element, encapsulation/functionalization material affect the sensing properties of magnetic materials.

Mainly two different sensing mechanisms are used to develop magnetic nanostructure-based biosensors (i) electrochemical sensing (ii) immune sensing. Electrochemical sensing methods are growing at a rapid rate as these devices satisfy several requirements for analytical detection and have a number of benefits like sensitivity, selectivity, rapid response, low cost, and electrochemical sensing approaches. Immunes sensing involves affinity ligand-based solid-state devices for biosensing, where the immunochemical reaction is connected to a transducer. All immunosensors are used to measure the specificity of how antibodies recognise antigens at the molecular level to create stable complexes.

The coating of chelating ligands on the surface of magnetic nanoparticles has been used to functionalize a wide range of materials. It has been frequently suggested to utilise stabilisers, electrostatic surfactants, and steric polymers to facilitate nanomaterials with non-specific, highly specific, or group-specific ligands. The stability of the colloidal suspension of iron oxide can be considerably increased by having their surfaces modified with the appropriate functional groups, such as carboxylic acids, phosphonic acids, and amines [60].

4.3 Carbon Based Materials

Carbon based materials including fullerenes, graphene and carbon nanotubes have attracted special attention of the scientific community for their potential applications in optical devices, catalyst support, quantum computers, biomedical applications, environmental sensors, pollution prevention strategy. Pure graphene sheets have limited application despite having excellent properties. Therefore, for practical applications in bio and environmental areas, introduction of controlled functional moieties over graphene producing graphene nanocomposites or hybrids are attracting interests. Carbon based nanocomposites can be utilized for sensing of inorganic ions, bio-organisms and biomolecule, bacteria and removal of toxic species from the environment [61].

The world population is growing very fast, thus, intensifying the agricultural and industrial activities, and in turn contaminating the environment including air, soil and aquatic ecosystem. Environmental and health issues have become a major focus of scientific and political attention. International effort is currently underway to comprehend how human activity affects the environment and to create new technology to lessen any negative effects on human health and the ecosystem. For the sensing of harmful metals like lead (Pb), Arsenic (As), mercury (Hg) and, several researchers have researched on graphene-based sensors with excellent sensitivity and quick response times.

Graphene is an excellent material for the development of sensors and biosensor-based devices in many transduction modes, from electrical and electrochemical transduction to optical transduction. Graphene is a transparent conductive material with a low cost and less effects on the environment. There are many oxygen-containing groups on its surface, thus helping with functionalization of the biomolecules for biorecognition events during biosensing as illustrated in Fig. 6.

Chen et al. [62] fabricated rGO nanosheets based field effect transistor conjugated with thioglycolic acid (TGA) functionalized Au nanoparticles for the detection of Hg^{2+} in aqueous suspension even at a low concentration i.e., 2.5×10^{-8} M. Results show that transistors do not show any sensing towards Hg (II) when fabricated without Au and TGA, respectively. This demonstrates the importance of functionalizing AuNP with TGA for giving rGO-AuNP-TGA nanocomposites the sensing activity. The carboxyl groups of TGA on AuNP surface interact with Hg^{+2} ions and result in variation in the concentration of charge carrier on rGO layers, responsible for the

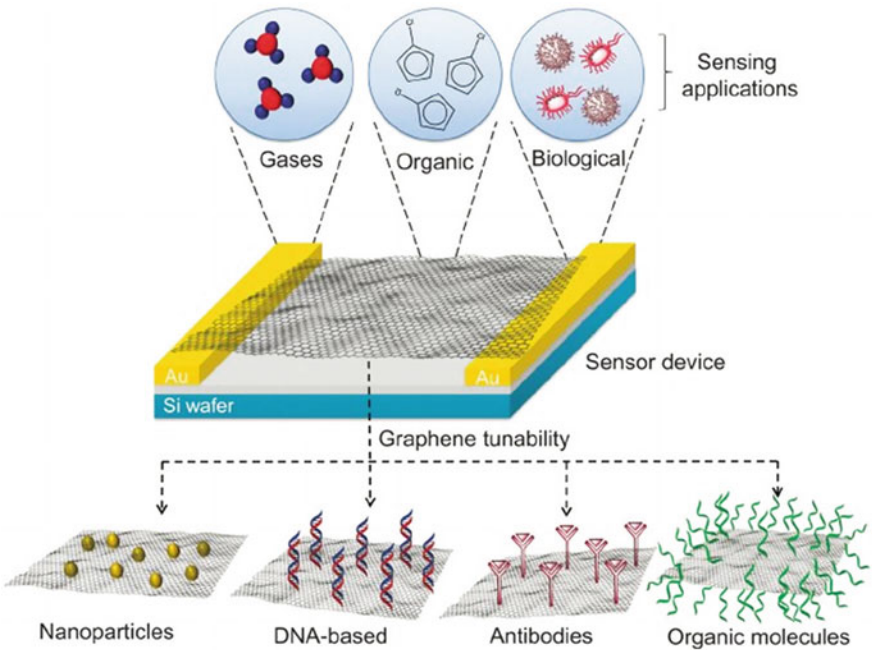

Fig. 6 Schematic exhibition of a graphene-based sensor showing its potential application as a platform for detection of organic molecules, gases, biomolecules and microbial cells. The sensing efficiency of graphene-based electrodes can be tuned by changing the surface chemistry of the graphitic materials through immobilization of metallic nanoparticles, polymeric compounds, DNA, and antibodies, and. Adapted with permission from [64]. Copyright (2015) Royal Society of Chemistry

rGO-AuNP-TGA composites' outstanding sensing capabilities. Liu et al. [63] have prepared functionalized graphene oxide and MONPs with DNA and proteins. They reported that the phosphate face and nucleobase face of DNA strongly adsorb on GO and MONPs surface. The results showed that with only the nucleobase backbone, the adsorption of proteins is strong on graphene oxide but not on MONPs surface. This type of knowledge will aid in the development of new intelligent nanomaterials based on DNA nanotechnology as well as DNA-based biosensors in complex biological samples.

4.4 A II–VI Nanomaterials

Another type of nanomaterial used for sensing application are the luminescent semi-conducting nanocrystals called Quantum dots. The most researched colloidal QDs from II–VI group including CdSe, CdTe, CdS, ZnSe, ZnS etc. as they provide a broad absorption spectrum and size dependent narrow emission spectrum. Nowadays QDs are available with reduced possible toxicity and offer functional groups over surface for the immobilization of bioreceptors with inert or biocompatible coatings [65]. Thus, as long as there is no effect on photophysical recombination properties, nearly any type of biomolecule can be conjugated to these nanocrystals.

Biosensors are also referred as smart systems as currently their development is based on the construction of small, fast, highly sensitive and selective and easy to use. Future research is focused on meeting the growing demand for improved sensitivity and selectivity, which will enable low-cost, real-time monitoring of chemicals. With all of the necessary components microfabricated on a chip, the future biosensor is anticipated to operate on the "laboratory on a chip" principle, making it simpler and extending dependable monitoring of the analytes outside the main laboratory.

The use of II–VI QDs is still limited because of the presence of heavy elements which causes toxicity to living cells. Thus, functionalization of II–VI nanostrcutures with biocompatible surfactants, polymers or biomolecules is of utmost importance [66]. Chen et al. [67]synthesized CdS QDs encapsulated with L-cysteine, polyphosphate and thioglycerol for the sensing of Cu^{2+} and Zn^{2+} ions. Results showed that QDs encapsulated with mercaptoacetic acid show high selectivity and sensitivity towards Cu^{2+} ions as compared to others by quenching the intensity of emission of QDs.

4.5 MXenes

MXenes are a class of 2D inorganic compounds first described in 2011 by Prof. Yuri Gogotsi [68]. The formula for MXenes is $M_{n+1}X_nT_x$, where M stands for the transition metal elements, X is an element of either Carbon or Nitrogen, n is one of 1, 2, or 3 (three common structures) and T_x is surface functional groups. The binding force between the MAX layer in the MAX phase and the A layer is weak, thus MXenes are mostly synthesized by selectively etching of the A element layers from tge MAX phase using suitable etching agents (e.g., HCl, LiF, HF, NH_4HF_2, etc.) at room temperature. The quality of MXenes is crucial in environmental application because the specific surface area of the material directly affect stheir adsorption and absorption abilities. It is a great carrier for biosensor applications since its surface may interact with most biomolecules through hydrogen bonding, electrostatic interactions, Van der Waals forces,, and ligand binding [69]. Many surface functionalization techniques, like as surface-initiated polymerization and single heteroatom doping, have been developed in recent years to increase the potential of MXenes in various applications.

The efficiency of MXenes can be improved easily by functionalizing with appropriate functional groups due to the hydrophilic nature of MXenes. MXene-based nitrite and glucose biosensors have been reported in the literature [70]. Functionalized MXene based membranes have been utilized for the removal of dyes from waste water and water, which is a top concern from an environmental standpoint [71].

4.6 Up Converting Nanoparticles

For bioanalysis luminescent labels and probes are crucial tool, however organic fluorophores are prone to photobleaching and quantum dots contains carcinogenic toxic metals. Most of the luminescent probes follow downconversion mode i.e., excitation with UV or visible light of lower wavelength and result in higher wavelength emission [72]. However, high energy light can cause photodamage and biomolecule autofluorescence, resulting in a low signal-to-noise ratio. The emission of upconverting nanoparticles (UCNPs) on the other hand is based on an anti-Stokes mechanism, which is the transformation of lower energy photons into higher energy photons. Although it does not allow for a direct functionalization, surface passivation by coating with a shell of (un)doped host material is frequently utilised to improve the overall upconversion efficiency. Silica shell is used to passivate the surface and introduces various functional groups over the surface via silanization [42]. During surface functionalization the properties of the host material can be altered, therefore along with the confirmation of the successful surface functionalization, it should also be noted that the modification does not have any negative impact on the upconversion efficiency or colloidal stability of the nanostructures. Various techniques can be employed to examine the functionalization, variations in the size and morphology of UCNPs, and their dispersibility in aqueous systems, depending on the kind of functionalization.

4.7 Metal Nanoparticles

To increase the life of metal nanoparticles and avoid undesired effects like aggregation in organic and aqueous solutions, physiochemical stability, and environmentally safe, it is important to choose stabilizing agents and surface functionalization approach that are environmentally safe, non-toxic and provide ease of fabrication [46]. Novel nanomaterial surfaces have many reaction sites and functional groups, which makes them effective adsorbents for efficient removal of heavy metal ions and adsorption reaction could be the likely mechanism. In an effort to enhance the biocompatibility and targeted specificity, the chemistry for the functionalization of noble metal nanoparticles (nanoparticles) with various biological moieties, such as antibodies, nucleic acids, biocompatible polymers, proteins, and enzymes has been advanced.

Among various metal nanoparticles, Au NPs are highly exploited for highly selective sensors. The local refractive index of AuNP patches functionalized with ssDNA complementary to the target microorganism DNA changes, and this change is visible using a spectroscope. This type of sensorcan be used to detect several bacteria and pathogenic fungi simultaneously. There are many "green" stabilising substances that can stable and functionalize metal nanoparticles without having an adverse impact on the environment or biological systems, including enzymes, polyphenols, citric acid, biodegradable polymers, vitamins (B, C, D, and K), and silica, to mention a few [73].

Currently, efforts are underway to discover effective methods for enhancing the properties of existing nanostructures materials and their potential biomedical applications. This field is incorporating a wide range of scientific and engineering disciplines and tools more than ever before. Despite significant progress made in modifying nanostructured materials for biomedical and environmental sensing applications, several challenges and technical obstacles still need to be overcome. The development of functional materials for biomedical and environmental sensing applications is a complex and challenging task that requires interdisciplinary expertise in materials science, chemistry, biology, and engineering. Some of the main challenges include selectivity, sensitivity, stability, cost effectiveness and biocompatibility. To address these challenges several approaches are being employed like designing of functional material with specific properties and functionalities by tailoring their chemical and physical properties including their size, shape and surface chemistry. Advanced fabrication techniques and synthesis of functional nanomaterials that mimic biological processes and structures, which can lead to more biocompatible and efficient sensors are being employed.

The development and use of functional nanomaterials for biomedical and environmental sensing applications have significant ethical and societal implications. The potential impact of this research is significant, both in terms of improving health outcomes for patients and reducing the economic burden of disease treatment, particularly in resource-limited settings. Nanobiosensors will enable the early detection of the deadly diseases and hazardous pollutants. But there is a need for robust regulatory frameworks to ensure that these materials are safe, effective, and reliable for their intended use. These materials may contain hazardous chemicals or require energy-intensive processes, which can contribute to environmental pollution and climate change. Therefore, it is important to engage in responsible innovation that considers the potential impacts of functional materials on individuals, communities, and the environment.

5 Conclusion

The development of nano sensors for the detection of environmental pollutants is accelerating, and as this chapter has shown, novel and inventive combinations of nanomaterials and recognition agents are constantly being developed. But bare nanostructures suffer from various challenges including stability in hostile environment, aggregation, bioaccumulation, toxicity etc. Thus, to overcome these limitations functionalization of nanoparticles surface is of utmost importance. One can predictably control and tune the characteristics of synthesized nanostructured materials through surface functionalization, and can also provide them biological features and functionalities to improve their compatibility with biomedical devices. There are numerous materials like polymers, surfactants, biomolecules used for the functionalization and stabilization of nanostructures used for sensing applications. Surface functionalization of nanostructures enhances the sensitivity, selectivity, solubility and efficiency of the sensing device for the detection of biomolecules and environmental pollutants. Although many advancements have been achieved till now in surface modifying technology but still there are some limitations and challenges remain. The future directions for the development and implementation of functional materials in sensing applications are focused on the integration of multiple functions, the development of smart and biocompatible materials, the use of sustainable materials, the integration of data analytics and machine learning, and the integration of multiple sensors. By pursuing these directions, researchers can develop functional materials that can address the current and future challenges in healthcare, environmental monitoring, and many other fields.

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Carbon Based Functional Materials as Hazardous Gas Sensing

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Abstract The rise of technology and the human population cause a variety of toxic chemicals and gases to form, which endanger all living things. Monitoring these harmful gas emissions is essential for keeping us safe in daily life. In order to detect harmful gases and vapours for environmental control, industrial monitoring, medical diagnosis, and domestic safety, gas sensors that are portable, flexible, and extremely sensitive are widely utilised. The development of materials that can react to lower gas concentrations in a remarkably short period of time has proven difficult. Nanomaterials have the potential to be developed into very efficient sensing technology due to the outstanding gas–solid interaction they show and the high surface-to-volume ratio. The currently available commercialized sensors are built on metal oxides, which typically operate at high temperatures and create extra challenges in the desorption of chemisorbed gas molecules. The interest in carbon nanomaterials (CNMs) among scientists has significantly increased during the past few years. They are highly intriguing for forming the next-generation of miniature, low-power, ubiquitous sensors due to their distinctive electrical, optical, and mechanical features. In particular, over the past few decades, the discovery of CNMs, such as carbon black (CB), carbon nanohorns (CNHs), carbon nano-onions (CNOs), nanodiamond (ND), carbon quantum dots (CQDs) carbon nanotubes (CNTs), graphene etc., has accelerated the study of gas sensors. More research has been done on CNM nanocomposites containing metal, metallic nanoparticles, metal oxides, and polymers to boost their selectivity, which shows better sensing capabilities even at room temperature. In this chapter, I will discuss the most recent developments in electrical gas sensors for hazardous gases employing CNMs and their hybrid/composites materials. Several papers including experimental and theoretical data will be reviewed and debated. For the discussions, the key findings for CB, CNHs, CNOs, ND, CQDs, CNTs, graphene with particular focus on the composites/hybrids of CNT and graphene with metal oxides, polymers, metals, etc. that exhibit sensing properties in many sectors will be taken into consideration. Finally, a future prognosis will be discussed, together with its highlighted difficulties and potential.

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1 Introduction

The modern way of life has a substantial negative influence on the environment due to the continuous emission of toxic gases that are invisible to the naked eye. Air pollutants including NO_2, CO_x, and CH_4 are mostly to blame for the damaging atmospheric changes resulting from environmental changes that have increased Earth's temperature [1–3]. Along with polluting gases, the environment also contains a number of additional hazardous gases, including CH_4, NH_3, H_2, and H_2S, which can explode when mixed in a specific ratio with air. A number of volatile organic compounds (VOCs), such as acetone, ethanol, toluene, and triethylamine (TEA), are harmful to human health in addition to these toxic gases. Thus, sensing these gases is crucial for environmental analysis, medical diagnosis, agriculture, public safety and security objectives etc. Consequently, there is a considerable need for gas sensors that are light-weight, portable, versatile, and affordable. There are different kinds of sensors, including chemiresistive [4], field-effect transistor (FET) [5], and micro-electromechanical system (MEMS) [6], depending on how they detect things. Among these sensing mechanisms, chemiresistive sensors have been extensively studied. For a variety of useful applications, metal-oxide sensors (MOSs) are currently well commercialized. These include hand-held ethanol sensors for cases of driving while intoxicated, methane and hydrogen sensors for the protection of workers in industries and mines, and acetone and toluene gas sensors for the diagnosis of diabetes and lung cancer [7]. For these practical sensing applications up until now, SnO_2, TiO_2, ZnO, CuO, In_2O_3, CdO, and WO_3 have received a lot of attention. These sensors have excellent sensitivity, but because of their high operating temperatures, they are more expensive to operate and maintain. Additionally, a modification to their surface shape impacts their sensitivity.

As a result, to resolve the aforementioned problems, CNMs like CB, CNHs, CNOs, ND, CQDs, CNTs, graphene, novel substitutes, have been investigated as sensing materials throughout the last two decades [8–11]. Compared to other commonly used materials, carbon nanomaterials provide a plethora of advantages. Due to their inherent electrical properties, which are sensitive to changes in the chemical environment, they stand out as the most important and optimistic choice for sensor manufacturing. Furthermore, they are suitable for high-efficiency chemical sensing because of characteristics including poor water solubility, good thermal and chemical consistency, low fluorescence and functionalization. More than 100 million unique compounds with various attributes can be created, thanks to their hybridization property, which enables the synthesis of several different chains with various lengths and electrical configuration [12]. Even while pristine CNMs have many benefits, they also have some significant disadvantages, including low selectivity, poor reproducibility, and irregularities in the functional groups on graphene derivatives or the number of layers [13, 14]. This has led to the exploration of nanocomposites of CNMs with metal and their oxides, organic materials, and polymers, and this novel class of CNMs hybrid sensing materials has showed exceptional performances without sacrificing their advantages. Additionally, CNMs have considerable flexibility [15, 16], making them suitable for use in the construction of wearable sensors.

In this chapter, I will discuss the most recent developments in the field of electrical gas sensors used for hazardous gases employing CNMs and their hybrid/composites materials. Several papers containing experimental and theoretical data will be examined and discussed. The main discoveries for CB, CNHs, CNOs, ND, CQDs, CNTs, graphene with particular focus on the composites/hybrids of CNT and graphene with metal oxides, polymers, metals, etc. that demonstrate sensing capabilities in numerous fields will be taken into account for the discussions. Finally, a prediction for the future will be discussed, along with its potential and any obstacles that stand out.

2 Mechanism

The conductivity change brought on by the transferring of charge between the target molecule and sensing layer is the fundamental process of chemical sensing. Due to their high surface-to-volume ratios, one and two dimensional nanostructures are especially suitable for this use. Therefore, even a modest charge shift at the surface can have a significant impact on how they conduct electricity. Gases can behave as holes or electron donors depending on their chemical structure. While p-type dopants like NO_2, boost conductivity by enhancing hole conduction, n-type dopants, like NH_3, deplete holes from the conduction band and cause a drop in material conductivity [17, 18].

Response time, recovery time, operating temperature, and sensitivity are four primary performance metrics used in the literature to assess sensors. Response time is defined as the time it takes for a sensor to attain 90% of its entire response, such as resistance, after being exposed to the target gas. Recovery time is defined as the time needed for a sensor to restore to 90% of its original baseline signal after removing the target gas. Sensitivity is defined as the ratio of a sensor's output signal change to a variation in the measured parameter. It measures how efficiently a sensor detects minor changes in the input signal. The operating temperature is the temperature range in which a sensor can work and produce accurate measurements.

A thin film's sensitivity or sensors response (R) is commonly computed using the formula:

$$R(\%) = 100 \times \frac{R_g - R_a}{R_a} = 100 \times \frac{\Delta R}{R_a}$$

Here, R_g is the film resistance when subjected to the target analyte and R_a is the film resistance solely when exposed to synthetic air. The sensing component, manufacturing procedure, and shape all play a significant role in how the sensor reacts when exposed to a particular gas.

3 Carbon Nanomaterials

Carbon nanostructures like CNTs and graphene are capable of sensing extremely low amounts of greenhouse and explosive gases. Therefore, using the gas sensitivity of graphene and CNTs to make highly sensitive, power-efficient gas sensors is of great interest to both industry and researchers. As a carbon nanomaterial for creating gas sensors, CNTs have recently attracted the greatest research attention. The supremacy of CNTs is currently being challenged by graphene, a carbon allotrope that has just recently been studied. However, nanotubes and graphene are not the only carbon nanomaterials used for sensing so for. Various other carbon nanomaterials such as CB, CNHs, CNOs, ND, and CQDs have also been studied. In this chapter, I will discuss the most recent developments in sensor technology based on the carbon nanomaterials i.e. CB, CNHs, CNOs, ND, CQDs, CNTs, graphene with particular focus on the composites/hybrids of CNT and graphene with metal oxides, polymers, metals, etc.

3.1 Carbon Black (CB) Based Gas Sensors

When gaseous or liquid hydrocarbons are burned insufficiently or thermally decompose under controlled conditions, colloidal particles of CB, which are almost entirely pure elemental carbon, are created. The CB in these sensors is spread inside the polymer and enhances the conductivity of the film. The polymer expands and ultimately changes in electrical conductivity and resistance when the required gas or vapour is available. The viscosity of the polymer/CB is appropriately adjusted using a suitable solvent before the polymer is patterned on the filter electrode's surface. The polymer is applied to the electrode surfaces using a variety of techniques, including spin coating and drops, before drying.

The notion of percolation is used to explain changes in a composite's strength as a function of the percentage of CBs [20, 21]. If the proportion of CB is low, the composite becomes insulated due to the lack of connections between the conductive nanoparticles in the composite body. The electrical resistance of the polymer reduces exponentially with increasing CB content [22–24]. The connection is established using the penetration limit by raising the CB concentration and travelling to the transfer point. When the required vapour or gas is available, the polymer expands and changes in electrical conductivity/resistance; this change is used to detect the gas (Fig. 1).

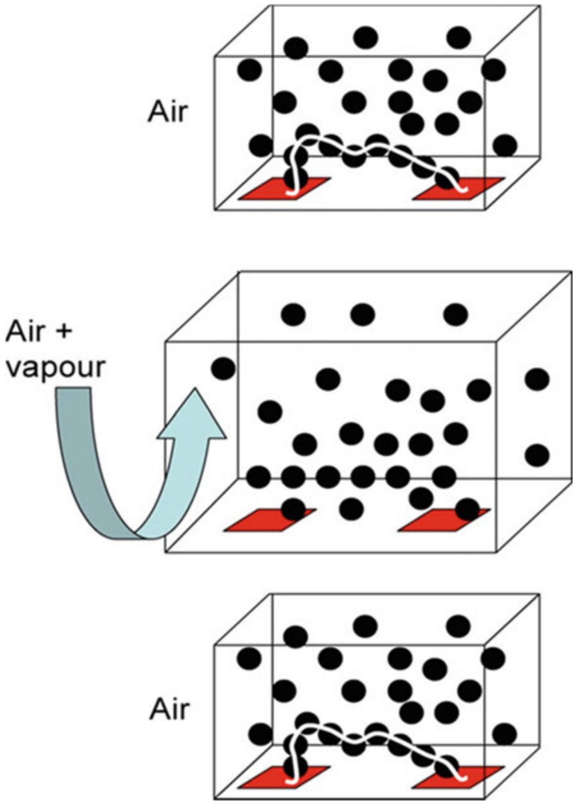

Fig. 1 Polymer/CB composite's gas detecting mechanism. The polymer matrix contains CB that has been dispersed in it. The conduction path between the electrodes is shown by the white line in the image above. This path and direction alter when vapours are present. The steering wheel returns to its initial position when fumes are eliminated from the atmosphere [19]. Copyright (2013) Elsevier

To respond to various vapours, Lewis and coworkers employed arrays of components, the team accomplished this using several polymer/CB composites. These arrays emit electrical resistance signals, which are assessed using a common system [25, 26]. The objective is to find different organic solvent vapours that may be present. This approach can be used with different hardware and software platforms to create a small, convenient tool that is also affordable.

Figure 2 displays, for instance, the sensory reactions for the detection of benzene and methanol. The responses will be moderate when these harmful gases are present in high concentrations. Due to deterioration polymer matrix or the displacement of CB particles, the polymer/carbon composite sensors may take longer to respond to external stimuli and may exhibit reduced sensitivity and stability over time. A diffusion path is caused by particle displacement or matrix ageing [27, 28]. The recurrent swelling and shrinkage of the polymer matrix brought on by the repeated operation of the sensor results in this change in configuration.

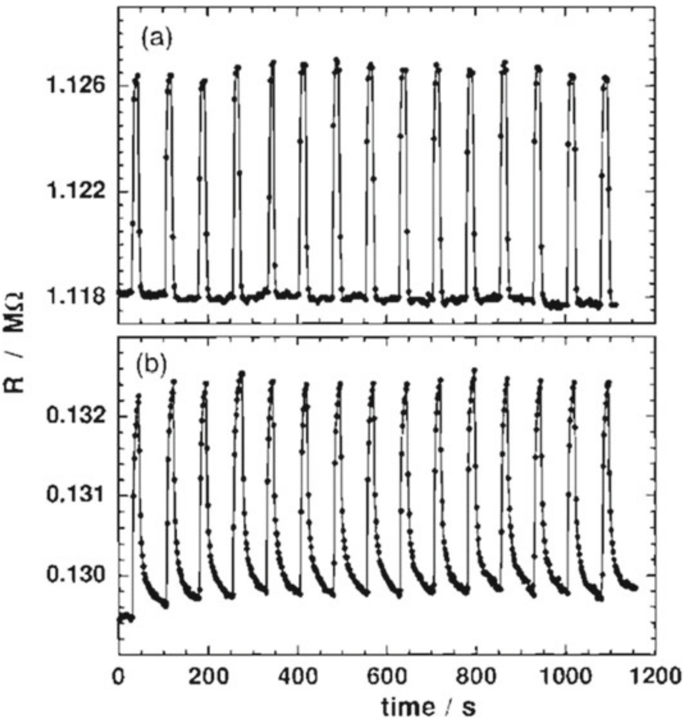

Fig. 2 Resistances of composite CB made of **a** poly(ethylene-co-vinyl acetate) and **b** poly(N-vinylpyrrolidone) after 15 exposures to benzene (1.1 ppt) and methanol (1.5 ppt). To show reproducibility and stability, exposures were spaced out between recovery times. Part per thousand (ppt) refers to the amount of airborne vapour in this context [29]. Copyright (1996) American Chemical Society

3.2 Carbon Nanohorns (CNHs) Based Gas Sensors

CNHs, a subclass of carbon nanomaterials with horn-like tips that mimic single-walled CNTs (SWCNTs), are depicted in Fig. 3. The main characteristic of CHNs is that they tend to form spherical clusters (dimensions: diameter; 2–5 nm, length; 40–50 nm) [30]. Flowers that resemble dahlias, buds, and seeds are the three different types of CNHs [31]. They are made by laser ablation of pure graphite at room temperature, which results in excellent yield and production rates, despite the fact that they have unique advantages like as increased surface area, improved electrical and thermal conductivity, and easiness in functionalization [32, 33]. CNHs are attractive prospects in a variety of applications [34] including biosensing, and gas sensors owing to their high surface area and many holes. The dielectrophoresis (DEF) technology was used by Suehiro et al. to create the CNHs gas sensor [35]. The performance of the CNHs sensor fabricated using DEP with respect to NO_2 and NH_3 gas was evaluated using impedance spectroscopy. Suehiro et al. demonstrated that CNHs can detect

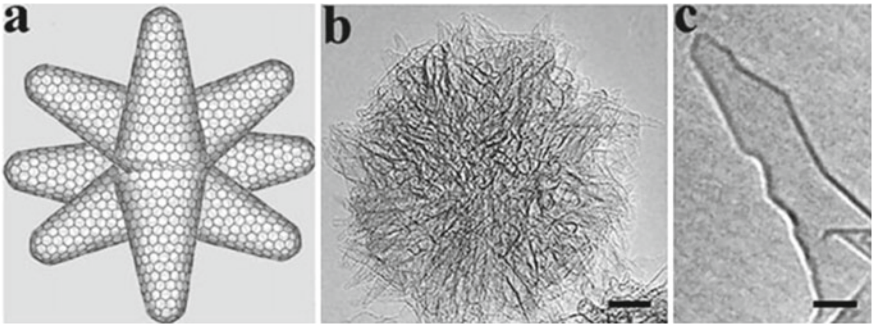

Fig. 3 **a** Shows a schematic of CNHs, **b** a high-resolution transmission electron microscope (HRTEM) image of the CNHs, and **c** a HRTEM image of a single carbon nanohorn with a size bar of 2 nm [38]. Copyright (2005) American Chemical Society

ppm-levels of NH_3 and NO_2 gases at ambient temperature [35]. Sano et al. examined the gas sensing properties of CNHs and presented a simple and affordable method for producing them. They established that the CNH's gas sensor can detect NH_3 and O_3 at room temperature. They discovered that under identical conditions, gas sensors made up of CNHs were more sensitive than sensors based on SWCNTs. They linked this improvement with monolayer gas adsorption as well as the interactions between adsorbed gas molecules that affect the charge transfer through gas molecules to the sensor surface [36]. With the oxidized nanohorns acting as an active sensing layer, the use of CNHs for humidity sensing can be expanded. Sensing capability was evaluated in nitrogen and air with a humidity range of 10–90%. The sensitivity in air is two times greater than the sensitivity in humid nitrogen. The presence of carboxylic groups can assist to explain this since interactions involving water molecules (being electron donors) reduce the amount of holes and oxidized single-wall CNHs produce increased resistivity [37].

3.3 Carbon Nano-Onions (CNOs) Based Gas Sensors

CNOs depicted in Fig. 4 are an allotrope of the fullerene-family of carbon nanomaterials, consisting of spherical, quasi-spherical, and polyhedral geometries with concentric graphitic shells [39]. The series C60@C240@C540@C960@C1500@C60n, where n denotes the shell number [40], can be used to define the many graphitic shell structures that make up CNOs. To create CNOs, a variety of synthesis techniques have been investigated, including thermal annealing of NDs, arc discharge, flame aided pyrolysis, chemical vapour deposition (CVD), and non-thermal plasma. The exceptional shell-shaped structure of CNOs may be the cause of their remarkable features, which include high specific surface area, incredible electrical conductivity, and good tribological behaviour [41]. The aforementioned characteristics of CNOs place them in the running for use

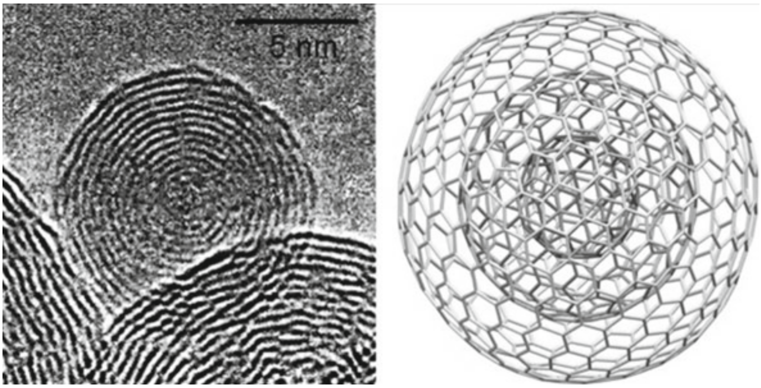

Fig. 4 Shows CNOs [42]. Copyright (2017) Elsevier

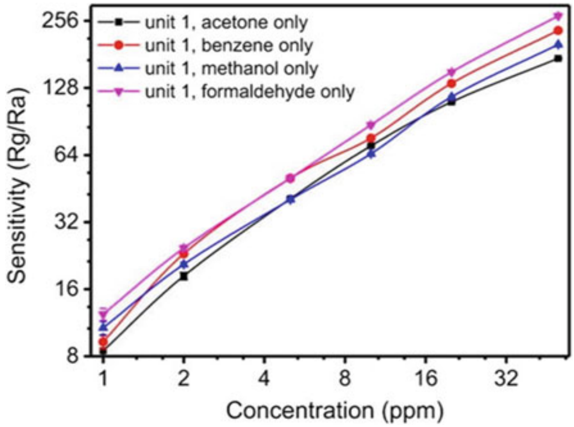

Fig. 5 Depicts, for a number of gases, the connection between sensitivity and gas concentration [43]. Copyright (2017) Springer Nature

as a material in a variety of applications, including gas sensors, supercapacitors, lubricants, electrochemical sensors, and optical limiting [39]. As far as I know, few investigations have been devoted to the CNOs' gas sensing capabilities. Dhonge et al. investigated the behaviour of CNOs in sensing volatile organic molecules (VOCs) at ambient temperature. Figure 5 illustrates how they demonstrated a linear relationship between sensitivity and gas concentration between 34 and 148 ppm [40].

3.4 Nanodiamond (ND) Based Gas Sensors

The zero-dimensional carbon allotrope known as (ND) is predominantly made up of carbon atoms arranged in short-range order tetrahedral sp^3 bonds [44, 45]. There are three primary industrial production technologies that can be used to produce ND. The first approach involves mechanically grinding high-quality diamond microcrystals made from graphite under circumstances of high pressure and temperature (HTHP), the second one is made up of explosive detonation synthesis and the third one is Chemical Vapour Deposition (CVD). The ND manufactured under harsh circumstances is present with particles ranging in size from 10 to 25 nm. According to XRD estimates, the usual crystallize size of ND generated by the detonation process is 4–5 nm [46]. The most common detonations, HTHP and CVD, have recently been seen as inferior alternatives to atmospheric pressure microplasma (AMP) [47]. Due to their exceptional chemical, mechanical, and optical properties, NDs can be employed in a wide range of applications, including gas sensors. In terms of gas sensing applications, the synthesis of MWCNTs was carried out using nanocrystalline diamonds employing CVD procedure. In a nutshell, the materials that were synthesized have a quick response time for H_2 gas detection. Furthermore, repeatability and selectivity were maintained throughout a two-month period. The increased response/recovery attitude may be attributed to increase in defect sites brought on by the presence of ND grains, which in turn encourages the creation of numerous hydrogen molecule binding sites [48].

3.5 Carbon Quantum Dots (CQDs) Based Gas Sensors

With a particle size of about 10 nm, the novel zero-dimensional carbon-based nanomaterial known as CQDs is easy to functionalize and exhibits strong fluorescence, high thermal stability, biocompatibility and an innocuous chemical structure [49]. CQDs upholds a considerable number of high criteria, including good photoluminance, simple preparation techniques, low cost, low degree of toxicity, and straightforward functionalization, to name a few. CQDs have recently been recognized as having applications in the sensing space with fine detection limits in the nano-, pico-, or even femto-molar range [50]. The standard hydrothermal technique is used to incorporate ZnO onto the matrix of CQDs to create a composite. Nitric oxide (NO) gas detection and monitoring are done using this compound. For a detection limit of 100 ppm, a recovery/ response time of 34 and 36 s, respectively, is captured. The silica aerogel functionalized CQDs are used to detect NO_2 in addition. The demonstrated selectivity of NO_2 gas among various gases, such as O_2, CO_2 and NH_3, is confirmed in this work [51]. In keeping with this carbon dot gas sensing, H_2S gas was detected utilising a specifically made Schottky apparatus using a composite of carbon dots reinforced with MgO nanoparticles. Both air and the gas being measured are used to evaluate the sensor's I–V inclination. The 120 ppm gas concentration naturally results in an increased response that is 11 times greater than the MgO at external voltage of −0.7 V. The reason why the aforementioned gas responded more strongly than other gases is due to the apparent decrease in barrier height that occurred during the H_2S gas exposure [51]. Graphene quantum dots produced utilising a straight forward solution manufacturing technique under ambient circumstances is used as an ammonia gas sensor. It's noteworthy to observe that two opposing current responses for the gas result from a flexible pH modulation from acidic to neutral [52].

3.6 Carbon Nanotubes (CNTs) Based Gas Sensors

The material for gas sensing applications that has gained the most research is the carbon nanotube. Gas molecules are more likely to bond to its surface due to its high aspect ratio, chemical, thermal, and mechanical stability, as well as its metallic and semiconductive qualities and functionalization capacities. In response to interactions with gas molecules deposited on them, CNTs experience a change in conductivity. They have the benefit of being able to detect the presence of gases at room temperature, as opposed to traditional metal-oxide gas sensors. The pure CNTs, on the other hand, have low selectivity, making it impossible for them to distinguish between various gases [53]. The sensing mechanism of pristine CNTs is also slightly troublesome since they frequently feature a combination of metallic and semiconducting tubes, in addition to the varied degrees of faults caused by the purification procedures. In light of this, alteration and functionalization have been suggested as a way to improve sensitivity and selectivity. CNT modification using different materials has been the subject of numerous investigations.

3.6.1 CNTs/Metals Gas Sensors

The effective detection of (Nitrogen Dioxide, Carbon monoxide, and Benzene) pollutants in CNTs embellished with gold nanoparticles is investigated using a mix of experimental and theoretical methods. In contrast to C_6H_6, where there was no discernible effect, gold nanoparticles show a direct impact on the detection of Nitrogen Dioxide and Carbon monoxide. By understanding the link between the Fermi level shift and the change in resistance following gas adsorption, this behaviour difference may be explained [54]. Additionally, rhodium nanoparticles were used to adorn CNTs added to these materials so they could function as sensors for the detection of Nitrogen Dioxide, Carbon monoxide, and Benzene. Because oxygenated vacancies serve as both anchoring sites for rhodium nanoparticles and active adsorption sites for gases, the presence of oxygen is crucial for enhancing gas responsiveness. It's also conceivable for CNTs and Ru NPs to transmit charge in a more direct manner [55]. Sharafeldin et al. added copper, platinum, titanium, Ruthenium and Cu, Pt, Ti, Ru, and silver to the MWCNTs to investigate their gas sensing behaviour. The MWCNTs/Cu nanocomposites were discovered to have the maximum sensitivity, measuring 1.75% when subjected to 10 ppm H_2S. Additionally, Sharafeldin et al. also showed that the MWCNTs/Pt responded more strongly, with a reaction of 1.96%, when exposed to 10 ppm NO_2 [56]. At ambient temperature, various quantities of carbon monoxide and NO were subjected to the zigzag MWCNTs decorated with palladium and Platinum nanoparticles. In order to study this unique structure, first-principles computations were used. According to a thorough investigation, SWCNTs adorned with Pt are more sensitive to carbon monoxide while those adorned with palladium are extremely sensitive to NO [57]. An NO_2 gas sensor was created using Au NPs with a regulated size and proportion over MWCNTs to detect low concentrations of NO_2 as low as sub-ppm. This research came to conclusion that the sensing capacities are controlled by the amount of Au nanoparticles deposited, the heights reaction to H_2S and the modest Au loading [58]. Ag/CNTs and ZnO/Ag/CNTs were deposited onto cellulose paper by Khan et al. using the simple and affordable spray method. Investigators reported that Ag/CNTs sensor responded more quickly and selectively to acetone than the Ag/ZnO/Ag sensor [59]. The CNTs with Ni NPs functionalized were created for the detection of SO_2, H_2S, and SO_2F_2. According to Gui et al., the Ni/CNTs sensor's low detection limit (LOD) against SF_6 was 1 ppm. H_2S, SOF_2, SO_2, and SO_2F_2 were shown to increase the sensitivity to various gases in that sequence [60].

3.6.2 CNTs/Metal Oxides Gas Sensors

Different physical and chemical methods have been used to anchor a range of metal oxide semiconductors to CNTs [61]. In order to improve CNTs' selectivity and sensitivity for use in gas sensing applications, the decorating process' main objective is to do so. In-depth study has been conducted on both SWCNTs and MWCNTs. The SWCNTs are set up as gas sensors for various toxic chemicals, including NH_3, NO, and NO_2. The SWNT-Fe_2O_3 composite film exhibits a steady response, improved sensitivity for H_2S, improved sensitivity for NO_2, and improved sensitivity at room temperature in comparison to pure SWNT films. These deformable, flexible sensors have a tremendous potential for wearable monitoring [62]. Research is being done on the use of ZnO and SWCNTs together to detect ethanol gas. On a copper substrate, the nanostructured materials were prepared using a spray pyrolysis technique. At a 6% weight concentration of ZnO/SWCNT, the best device performance is visible. Chemisorption, which achieves the transfer of charges between the adsorbed gas species and the metal oxide surface, is what produces the gas sensor response [63]. The same SWCNTs covered ZnO produced using a wet chemical process is also used to construct gas sensing for nitrogen dioxide, with response and recovery times of 70 and 100 s, respectively. The ideal sensing conditions are attained at 150 °C and 1000 ppm nitrogen dioxide [64]. The electrochemical synthesis method is also used to evaluate gas sensing utilising ZnO/SWCNT hybrids. Performance is carried out at room temperature for a number of gases, including CO, CO_2, NO_2, H_2S, O_2, and NH_3. By precisely altering the electrochemical variables, density, crystallinity, and eventual particle size, a correlation between the gas sensing behaviour and the ambient conditions is seen. In summary, compared to the non-functionalized MWCNTs, the functional ZnO/MWCNTs exhibit approximately 5% per ppm for the H_2S gas.

A practical sol–gel approach was used to create SnO_2 and TiO_2 carbon nanotube mixtures for ethanol detection. Within a broad temperature range of ambient temperature to 250 °C, the mixture exhibits good qualities such as thermal stability and enhanced sensitivity [65]. Vanadium oxide-filled MWCNTs were used to illustrate the utilization of physical attributes as well as gaseous tracking. The composite's methane gas detection response at room temperature approached 16 s due to an increase in state densities among Fermi energy levels. In CNTs-based sensors, the influence of atmospheric oxygen was stressed and highlighted [66]. Cháfer et al. investigated the possibility of employing an IrOx-MWCNT nanocomposite for simultaneous NO_2 and NH_3 detection. Cháfer et al. demonstrated that, in comparison to pure MWCNTs, IrOx-MWCNTs nanocomposite can detect NO_2 and NH_3 at various working temperatures exhibiting good reproducibility, stability, increased sensitivity down to 1 bbp, and lower noise levels [67]. ZnO that has been doped with MWCNTs is used for toluene based gas sensor. In a nutshell, a variety of ZnO/MWCNTs that were produced via the reflux method is presented. MWCNTs make it difficult to prepare agglomerations for ZnO nanostructures. The 3:1 ratio of ZnO to MWCNTs results in a 17% increase in the sensor response at 150 °C compared to pure ZnO, which has no response at the given temperature [68]. In another report, Sonker et al. reported efficient LPG gas sensor based on MWCNT Doped ZnO Nanocomposite Thin Film [69].

T. Guo et al. created the ammonia gas sensor that operates at ambient temperature. They employed a CNTs/Fe_3O_4 combination to discover a lower content of ammonia at ambient temperature. At ammonia concentrations of 20, 40, 60, and 80 ppm, they put the CNTs/Fe_3O_4 sensor to the test. The findings conclude that the sensor has a quick recovery time and responds selectively to ammonia. In addition to these benefits, as demonstrated in Fig. 6, the sensor also exhibits strong linearity, robust repeatability, and high stability [70]. ZnO nanostructures with MWCNT decorations are ready for hydrogen gas detection. Performance is increased by using Pt nanoparticles sputtered onto the composite surface. 78 s recovery times are attained for 0.05% of the targeted gas at room temperature, together with good reproducibility and stability. Furthermore, the MWCNTs/ZnO/Pt reaches 4% sensitivity, approximately twice that of the MWCNTs/ZnO [71]. The conventional chemical precipitation method was successfully applied to create the Al_2O_3/CeO_2/MWCNTs nanostructure under the impact of an ultrasonic wave for CO_2 gas. According to the data collected, the response and recovery times of the thermal conductivity sensor are 9 and 13 s, respectively, and are comparable to those of the majority of commercially available CO_2 sensors [68]. The as-synthesized MWCNTs/ZnO using reflux technique at ~197 °C in ethylene glycol is employed for methanol gas detection. A wide range of temperatures between 100 and 300 °C were explored for the sensing behaviour, with the latter temperature yielding the best results. For the purpose of methane detection, Al_2O_3 doped with MWCNTs is also offered [72].

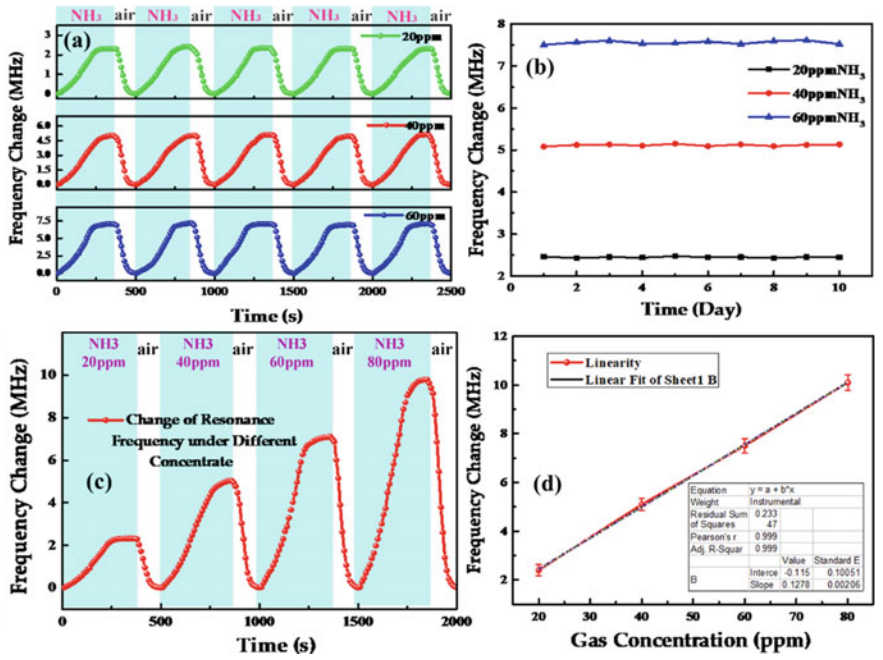

Fig. 6 Shows the **a** repeatability, **b** stability, **c** responsiveness at various concentrations, and **d** linearity of the CNTs/Fe_3O_4 gas sensor [70]. Copyright (2018) MDPI

3.6.3 CNTs/Organic Materials Gas Sensors

Gas sensors for detecting volatile organic chemicals were made using CNTs and poly-ethylene glycol (VOCs). At room temperature, it was possible to achieve viable high response (110 s) and recovery (152 s) rates in different concentrations of acetone, isopropanol, isoprene and ethanol. These rates [70] characterize the sensor as a portable electronic-nose device [73]. As a sensitive material, poly (3,4-ethylenedioxythiophene) polystyrene sulfonate-multiwall CNTs can also be used to advance gas sensing. By integrating a sensing platform tailored to low power applications with the Internet of Things, this research intends to deliver a low-cost communicative sensor [74]. NO_2 gas detection is performed by using single-walled nanotubes positioned on the flexible polytetrafluoroethylene (PTFE) filter substrate. A good stability of sensitivity was demonstrated when the substrates were bent repeatedly between 0.75 and 2 ppm concentrations. However, a substantial increase in sensitivity was found for concentrations of 3–5 ppm. The porousness of the substrates may have something to do with this. The sensitivity of the sensors can be doubled when compared to those made over a silicon substrate. Additionally, the electron-donor nature of water molecules causes a reduction in sensitivity at 10 and 30% humidity. These findings are helpful for flexible electronics and air quality monitoring [75].

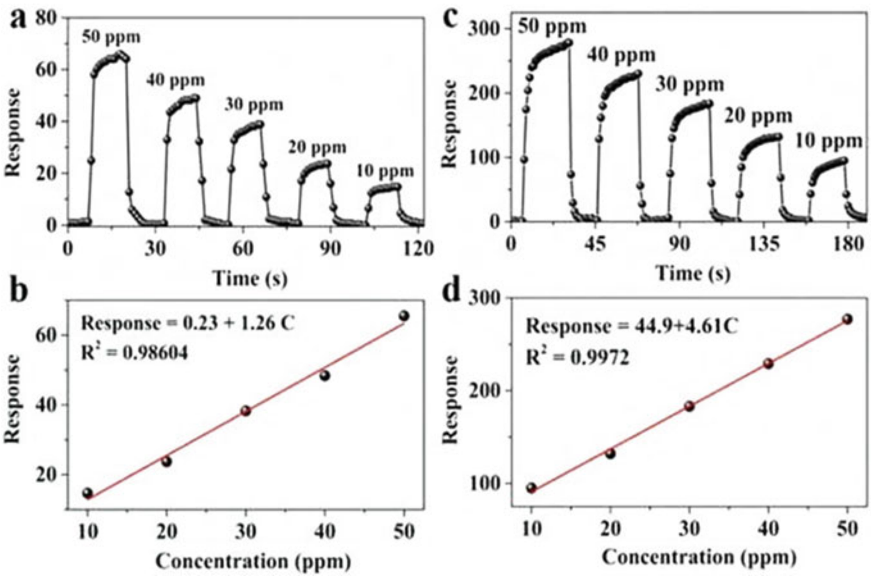

Fig. 7 Illustrates the **a** response of the p-PANI/CNT sensor to NO_2 gas, **b** a sensor's reaction to NO_2 concentration fit curve, **c** responses to NH_3 gas and **d** a fitting curve of the sensor's response to NH_3 concentration [78]. Copyright (2020) MDPI

Ammonia gas is detected using CNTs and polyaniline films. Sulfuric acid, camphor sulfonic acid and m-cresol were used for doping. Among which the sensing capability of camphor sulfonic acid was optimized and found equivalent to other responses. This is due to both the conservation of the initial volume of polyaniline and the evenly dispersed polarons induced by the concerned doping agent. This device works with improved sensitivity for ammonia gas detection, with a 4 ppm detection limit [76]. An acetone gas sensor made of a composite sheet of polyethylene glycol (PEG) and MWCNTs was demonstrated by Chiou et al. PEG/MWCNTs were more sensitive under mild temperature than they were in the lack of the thermal treatment, which is desirable for environmental applications, according to the results of the sensing performance tests [77]. W. Zhanget al. looked at how well the PANI/CNT composite worked for monitoring NO_2 and NH_3. To improve the sensing capabilities of the PANI/CNT composite, they developed a core–shell structure using n-type PANI and p-type MWCNTs. The low detection limits (LOD) for NO_2 and NH_3 were found to be 19.6 and 6.5 ppb, respectively, as depicted in Fig. 7 [75].

3.7 Graphene Based Gas Sensors

One sheet of carbon atoms arranged in a hexagonal lattice is called graphene, and it has also been used to detect gases. With detection limits as low as ppb [14], graphene-based materials are good candidates for chemical sensing. However, additional precautions must be taken to prevent surface contamination brought on by the lithographic process [77]. This is a result of their inherently low noise structure, substantial specific surface area, and remarkable carrier mobility, which are all distinctive characteristics. Gas sensing performance of graphene can be considerably enhanced by the proper functionalization, according to theoretical and practical investigations. As in CNTs, dopants or defects also increase the adsorption energy in graphene which improves the sensitivity and selectivity. The interactions of four different forms of graphene (pristine, B- or N- doped, defective, and flaws) with minute gas molecules (CO, NO, NO_2, and NH_3) were investigated in order to investigate the potential of graphene as a gas sensor [79]. GO, reduced GO (rGO), and functionalized rGO conductometric devices have all been reported to have strong gas sensing capabilities [80–82]. Recently, graphene composites with other materials have shown tremendous sensing capabilities. The following section will discuss the composite/hybrid of graphene briefly.

3.7.1 Graphene/Metals Nanocomposite Gas Sensors

GO-metals have recently attracted a lot of attention due to their improved catalytic, electrical, and optical specifications [83]. Utilizing the Pt–Pd/rGO, hydrogen gas detection is carried out. It is established that the response is stable and repeatable. This could be explained by the crystal lattice expansion and carrier donation that occur during hydrogenation and dehydrogenation. By raising the hydrogen content or lowering the operating temperature, the responsiveness can be improved. No discernible changes in the sensor result are reflected in the flow rate variation. Higher response/recovery durations were attained when nitrogen was used as a gas carrier rather than air. This might be viewed as the reaction's oxygen contribution [84]. NO_2 sensing is brought up by addressing the impact of electron beam exposure on Pd-fortified rGO composites. A range of irradiation dosages, from 0 to 500 kGy, were used; the latter level produced the best results. A reaction time of 345 s was measured at a NO_2 concentration of 10 ppm, however the recovery time for the same concentration and dose is 816 s. This enhanced gas reaction is brought on by high energy defects and the abundance of oxygen functional groups [85].

The hydrogen gas is detected using a Pd/rGO hybrid. The hybrid was created with the use of microwave irradiation. From ambient temperature to 120 °C, a wide temperature range was used to examine sensing performance. The 1% H_2 sensing at 100 °C resulted in the greatest response of 14.5%. The increased interaction between hydrogen molecules and the sensor layer may explain this observation [86]. Reduced graphene oxide adorned with silver, gold, and platinum nanocomposites, which were made via a one-step chemical reduction technique, are also used to detect ammonia gas. Silver displayed the highest recovery, responsiveness, and sensitivity among these three nanoparticles [87]. In recent research, NO_2 detection using graphene with an Au decorated porous structure was accomplished at a standard ambient temperature. When gas concentrations drop to 50×10^{-9}, the sensor still responds within 30 s. The sensitivity was increased by au ornamentation to about 1.5 times that of clean graphene [88]. Ag-$MoSe_2$/rGO ternary composites were used for hydrogen sulfide gas sensing. At room temperature, several values ranging from 0.1 ppm to 30 ppm were investigated. According to studies on how the potential barrier is regulated during electron transport and how the ternary composite structure works in concert, adding Ag to the compound appears to have an impact [89].

3.7.2 Graphene/Metal Oxide Nanocomposite Gas Sensors

For use in sensing applications, metal oxides such as ZnO, MnO_2, WO_3, MoO_3, and CuO are extensively researched. On the one hand, these oxides have raised surface specific area and reasonable flexibility, but on the other hand, they do not have adequate electrical conductivity. By combining metal oxides with graphene and its derivatives, electrical conductivity can be naturally increased, which enhances sensor performance. There have been reports of graphene and metal oxide introduction [90]. The addition of metal oxides to graphene causes new physical and chemical properties to develop. Furthermore, it plays a crucial part in preventing the formation of aggregated graphene sheets. For the hydrothermal approach of methane detection and sensing, the nanocomposite of NiO/rGO was introduced. The sensing mechanism was proposed to be the Fermi energy band between NiO sheets and rGO nanoparticles. For concentrations between 100 and 500 ppm, long response times of roughly 6–18 s were observed [91]. In order to detect formaldehyde, Weiwei Guo et al. used a ZnO-rGO nanocomposite that they synthesized using a one-pot hydrothermal process and ZnO that was doped with Fe. The inclusion of Fe causes the ZnO hexagonal prism of the ZnO-rGO nanocomposite to shrink, while also increasing the ZnO's surface area. Response-recovery times for a formaldehyde concentration of 12–5 ppm are maintained with a Fe doping of 5% [92]. ZnO treated with rGO was used for ultrasensitive monitoring of NO_2 gas. The reaction at 100 °C is approaching a seven-fold improvement over pure ZnO. 5 ppm is the lowest detection limit that has been attained. The enhanced performance of the sensor is attributed to p-n heterojunctions between the ZnO and rGO [93].

The hydrothermal method of production was used to obtain the rGO-TiO_2 nanocomposite for ammonia sensing. In order to acquire the rGO-TiO_2 nanocomposite with the intention of ammonia sensing, the hydrothermal method for preparation was introduced. At ambient temperature, the aforementioned nanocomposite showed improved selectivity and sensitivity for ammonia concentrations as low as 5 ppm [95]. But even at lower 100 ppm concentrations, the same nanocomposite can detect CO gas [96]. The rGO/ZnO nanocomposite was created by Vardan Galstyan et al. to detect H_2, CH_4 and NO_2 gases. The resultant composite's conductivity is increased by the addition of rGO, which enhances the response to Nitrogen dioxide and Hydrogen gases as seen in Fig. 8. In contrast to pure ZnO, the rGO/ZnO nanocomposite reacts to NO_2, gas preferentially at surprisingly low operating temperature [94].

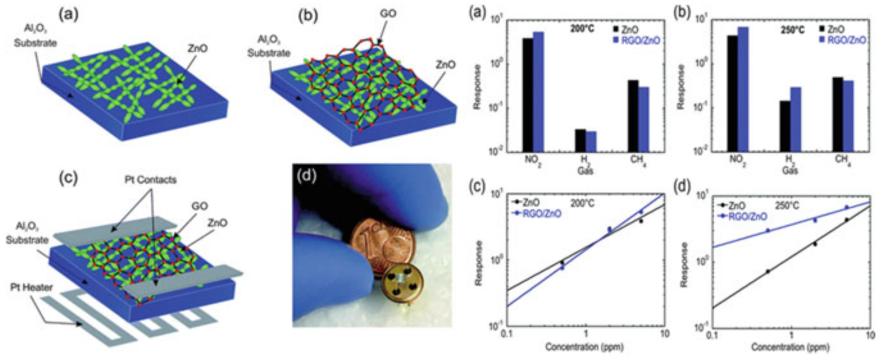

Fig. 8 Shows a schematic of how a gas sensor device is fabricated [94]. Copyright (2016) Royal Society of Chemistry

GO-WO_3 nanocomposite films are used to demonstrate the detection of another gas (in this example, NO_2). Combining the polyol method with metal–organic decomposition was used to carry out the synthesis. It was confirmed that there was immediate sensitivity within 0.5–5 ppm and excellent repeatability. Long-term stability for more than a month has been documented at room temperature [97]. The decoration of CuO with rGO was used for CO detection using the layer-by-layer method of self-assembly. The investigation covered a broad range of CO concentrations, from 0.25 to 1000 ppm. It was shown that the constructed heterojunction at the copper oxide–reduced graphene oxide interface produced excellent performance in terms of repeatability, sensitivity, and stability. SnO_2-GO nanocomposite shown acknowledged sensitivity to detect NH_3 with 10–50 ppm at ambient temperature [98]. The rGO-Fe_3O_4 nanocomposite is also used for carbon monoxide sensing; response-recovery periods of 32–35 s are obtained for a 5 ppm concentration, respectively [99]. Another method of carbon monoxide gas detection for NiO/graphene was provided using hydrothermal reflux technology [100]. For the purpose of monitoring H_2S and SOF_2, a hydrothermal process was used to generate SnO_2-rGO nanocomposite. The ideal circumstances lead to the cleanest rGO sensors. For concentrations of 100 ppm H_2S and 10 ppm SOF_2, respectively, enhanced responses of 34.31 and 3.13% higher than those of a pristine rGO sensor at 125 °C were attained [101]. It was successful to create a rGO-SnO_2-Au tri-structure system to identify formaldehyde. A remarkable increase in sensor responsiveness and selectivity was possible. This enhanced reaction could be attributed to the increased surface area, the catalytic action of the Au nanoparticles, and the ohmic contact synergistic interaction between SnO_2 and rGO [102].

3.7.3 Graphene/Polymers Gas Sensors

With the use of rGO/polymer nanofibers, nitrogen dioxide was monitored and detected. A high sensitivity of 1.03 ppm and room temperature applicability were conceivably attained. Additionally, the electro-spun technique of synthesis provides a workable, environmentally friendly, and reliable path for preparation [103]. The detection limit of 150 ppm was also reached. The combination of rGO/conductive polymers was proposed as a potential tool for the Langmuir-Schaefer (LS) method to develop ammonia sensors. The four synthesized compounds showed the highest pyrrole-rGO-polyaniline sensitivity when pyrrole (Py) was utilised as the reducing agent. The detection limit was held at 0.2 ppm [104]. A graphene/ethyl cellulose nanocomposite was designed to provide a wearable gas sensor that is very sensitive and has a reduced strain response. At the minimum bending radius of 3.18 mm, this sensor exhibits a comparable resistance differential of 0.3% after 400 cycles of bending. For a 5 mm bending radius, 0.2% resistance change was attained. Monitoring was also done for detection limits, which ranged from 37 to 167 ppm. It was noted that ethanol, acetone, IPA, and hexane were detected [105].

3.7.4 Graphene/CNTs/Metal Oxide Nanocomposites Gas Sensors

Research is also being done on the nanocomposite of CNTs and derivatives of graphene that is used in gas sensing applications. These composite materials include NO_2 gas sensors made of CNTs and rGO. These sensors have a flexible polyamide substrate and operate at ambient temperature. Both their great sensitivity and high bending ability have been noted for these sensors, with the former being attributed to the presence of CNT arrays while the second being credited to the remarkable flexibile nature of graphene sheets [106]. According to recent research by Morsy et al., the nanocomposite in combination with ZnO generated using the conventional precipitation method facilitates the detection of ammonia at ambient temperature. For the gas that was found and is currently under study, longer response and recovery periods were observed [107]. Vibha Srivastava et al. discovered that graphene/SnO_2 synthesized using the sol–gel process has a greater intrinsic gas sensing response for NO_2 than graphene/MWCNTs/SnO_2 at ambient temperature. Reduced response times of less than one minute and a recovery period of almost five minutes are indicators of the composite. The increased reaction might be attributed to the surface's complete exposure to the environment [108].

3.7.5 Graphene Foam and Three-Dimensional Graphene Gas Sensors

In addition, three-dimensional (3D) graphene foams are used for the detection of glucose employing the electrochemical sensing approach. The electrode scaffold was made of macroporous 3D graphene foam produced by chemical vapour deposition (CVD). A broad linear range (5–65 M) is used to reach the lowered detection limit of 1.5 M [109]. In a different report, a macro graphene foam-like material is used to detect gases. Here, there is a fusion of acceptable reliability and great sensitivity. Only a few ppm levels of NH_3 and NO_2 gases could be detected in the ambient air. Additionally, the proposed combination utilises less energy compared to Joule-heating, which combats molecules that have been chemisorbed off the surface of the foam, and produces an adequate level of mechanical strength and flexibility [110]. The ability of the three-dimensional reduced graphene oxide (3DRGO) decorated with ZnO nanoparticles to detect CO gas was investigated. The work by HaiHa et al. demonstrated that the sensor based on 3DRGO/ZnO has a rapid response and recovery, stability, good linearity and enhanced selectivity [111]. 3D graphene that was loaded with Co_3O_4 was used to detect VOCs. The GF/Co_3O_4 nanocomposite demonstrated great responsiveness and rapid response time at low Xylene concentrations [112].

4 Current Challenges and Outlook

Despite their high sensitivity, nano-carbon based sensors have a number of drawbacks, including limited repeatability, cross-sensitivity, irreversible recovery, non-uniform dispersion, defects, and low functional group stability, which necessitates further research and development before they can be commercialized. Different hazardous gases require gas sensors to have an extremely low detection limit. People might be warned about possible exposure to dangerous conditions beforehand using an ultralow detection limit as low as ppb. Future research should focus on developing gas sensors that are more sensitive, selective, and have lower detectivities for the intended gas analytes: (a) in order to improve gas sensing performance and achieve higher sensitivity, techniques like size control, doping, chemical modification, use of additional materials to modify functionality and defect generation and control have demonstrated their high efficacy. Through the use of these techniques, the interactions between analytes and sensing materials can be improved, resulting in a more sensitive reaction to the chemisorption or physisorption of molecular analytes; (b) in order to lower the detection limit of gas sensors, which is primarily determined by the sensitivity and resolution of the sensors, it is possible to increase surface areas, enhance material-analyte interactions, functionalize sensing materials, and employ analytical techniques; (c) for the selective detection of one or more analytes of interest, suitable host–guest hybrid material combinations can be used and created, improving the selectivity of gas sensors.

5 Conclusion

Traditional metal oxide semiconductor sensors offer several benefits and some limitations. The new class of sensors, which rely on nanoscale materials, are predicted to have some advantages over traditional sensors. As a result, carbon nanomaterials possess a number of outstanding mechanical, optical, electrochemical, and electrical features that make them suitable for use as sensors, either by themselves or in combination with other substances. This sensitivity to changes in their immediate chemical environment is one possible explanation for why these kinds of nanomaterials exhibit such sensitivity. This could be explained by the way that molecules that interact have an electrical structure. They are the ideal materials for sensing gases because of their sensitivity. In this book chapter, I covered the implications of carbon-based nanomaterials for gas sensing. I began with an introduction that features CB, CNHs and nano-onions before moving on to NDs and CQDs. Further I discussed about the sensing capabilities of CNTs and various CNTs combinations. This study outlines the enhanced detection limits and response/recovery timings for CNTs/metals, CNTs/metal oxides, and CNTs/organic materials in gas sensing performance and evolution. Finally, I discussed graphene-based gas sensor combinations including graphene/noble metals, graphene/metal oxide, graphene/polymers, and graphene/CNTs/metal oxide. I had covered a progression of the debate from 0D, 1D, 2D, and finally 3D foam graphene. Finally, the key lessons for selecting the best carbon-based materials along with the consequences for forthcoming challenges and outlook are discussed.

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Carbon-Based Functional Materials for Optical Sensors

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Abstract The development and innovation of carbon-based functional materials have led to a wide range of structures, increasing the interest in finding and exploring new avenues for the synthesis of nanomaterials. This has enabled the development of diverse materials with different applications, contributing to their inexpensive production and widespread use. Carbon-based functional materials exhibit excellent properties such as high strength, high density, and high hardness, making them ideal for various applications. Functional materials are materials with specific properties that can be used in various applications, and they are often used in sensors to enhance their sensitivity, selectivity, and response time. Semiconductors, piezoelectric materials, optical materials, magnetic materials, and nanomaterials are common functional materials used in sensor applications. The use of functional materials in sensor design plays a critical role in achieving high sensitivity and selectivity. Carbon-based functional materials are increasingly used in sensor design due to their advantageous intrinsic properties, including high electrical and thermal conductivity, chemical stability, large specific surface area, optical properties, biocompatibility, and simple functionality. Graphene, carbon nanotubes, fullerenes, and carbon nanofibers, including their functionalization with polymers, metal oxide nanoparticles, silica, and other materials, are examples of carbonaceous nanomaterials used in sensors. The prospects for novel applications of carbon-based functional materials are vast, ranging from energy, catalysis, environmental science, biomedical, optoelectronic infrastructure, vehicle transportation, security and surveillance, land resources and environmental monitoring, military, industrial, oil/gas/minerals exploration and refining, power generation and distribution, medicine/health/and biotechnology, food

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technology, home and mobile wearable devices, space, and optical communication. This chapter focuses on the optical sensor and its wide range of carbon-based functional materials, which have revolutionized the field of sensor technology for the development of ever more sensitive devices. This work aims to provide a detailed study of their properties, research, and development of new technologies to minimize the current serious environmental impact.

Keywords Carbon-based functional materials · Carbon dot · Carbon nanofibers · Carbon nanotubes · Diamond · Graphene · Optical sensor

1 Introduction

The development and innovation of carbon-based functional materials have led to a wide range of structures, increasing the interest in finding and exploring new avenues for the synthesis of nanomaterials. Figure 1 shows that carbon-based functional materials (CBFM), such as graphene, carbon nanofiber, graphene/metal oxide, carbon quantum dots (CQDs), carbon nanotubes (CNTs), and carbon dots (C-dots), have emerged as promising candidates for optical sensing applications due to their unique optical, electrical, and mechanical properties [1, 2].

Optical sensing is a non-destructive analytical technique that measures changes in the optical properties of a material in response to the presence of an analyte. Optical sensors have gained significant attention due to their high sensitivity, selectivity, and

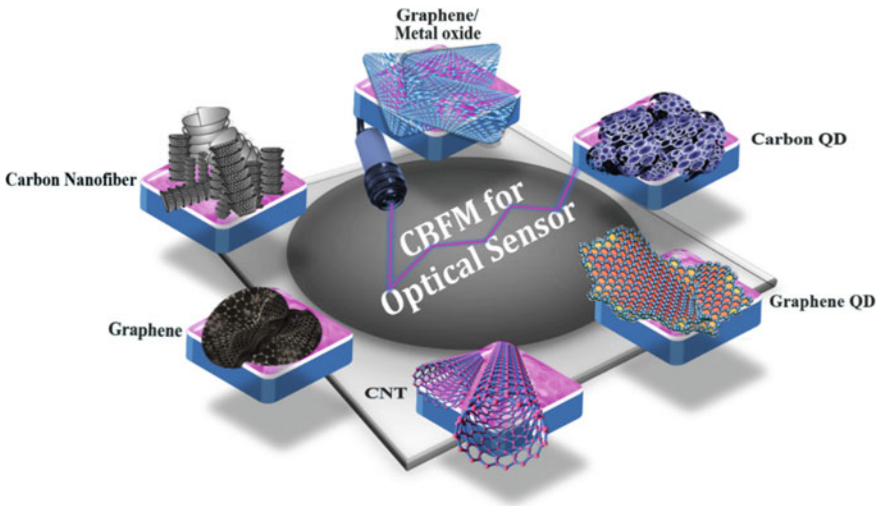

Fig. 1 Different carbon-based materials and their unique structures for use in optical sensor applications. © Sohel Shaikh, (2023) All rights reserved

real-time detection capabilities. CBFM, such as graphene, carbon nanotubes, and carbon dots, have unique properties that make them attractive for various applications, including optical sensors. In this chapter, has provided a comprehensive study of the recent progress in the development of CBFM for optical sensing applications.

Here are some key milestones in the development of carbon-based materials for optical sensing applications:

- In the early 1990s, researchers discovered CNTs, which are cylindrical carbon structures with unique electronic and optical properties. In 2000, researchers demonstrated the first semiconducting single-walled CNTs-based gas sensor, to detect the presence of NO_2 and NH_3 with high sensitivity [3].
- In the mid-2004–2006, researchers began to investigate the use of C-dots, which are fluorescent carbon nanoparticles, as sensing elements in optical sensors. C-dots have been shown to be highly sensitive to various analytes, including metal ions, organic compounds, and biological molecules [4].
- In 2010, researchers Geim and Novoselov were awarded Nobel Prize for their pioneering work regarding two-dimensional atomic crystals with high electrical conductivity and transparency. Since then, graphene has been studied extensively for its potential in optical sensing applications due to its unique electronic and optical properties [5].
- In recent years, researchers have also explored the use of other carbon-based materials, such as carbon fibers and diamond, for optical sensing applications. Carbon fibers have a high surface area and can be coated with sensing materials to enhance their selectivity and sensitivity. Diamond, being transparent and electrically insulating, can be functionalized to detect different types of analytes.

The CBFM is a diverse group of materials that share the common feature of being composed primarily of carbon and having unique properties that make them suitable for various applications, including optical sensing. Optical sensors use the interaction between light and matter to detect different types of analytes, such as gases, liquids, and biological molecules.

The CBFM can be used as sensing elements in optical sensors due to their unique electronic, optical, and surface properties. CNTs are highly sensitive to changes in their surroundings and can be functionalized with various molecules to enable selective detection of specific analytes. Similarly, graphene has been shown to exhibit strong interactions with analytes, leading to changes in its optical properties that can be used for sensing purposes.

Other CBFM, such as carbon dots, carbon fibers, and diamond, also have unique properties that make them suitable for optical sensing applications. Carbon dots, for instance, have fluorescent properties that can be used for sensitive detection of biomolecules and other analytes. Carbon fibers, on the other hand, have a high surface area and can be coated with sensing materials to enhance their selectivity and sensitivity. Diamond, being transparent and electrically insulating, can be functionalized to detect different types of analytes [6].

Nowadays, CBFM continues to be an active area of research in the field of optical sensing. Ongoing efforts are focused on developing new materials with enhanced sensing properties, optimizing the design of optical sensors, and exploring new applications for these materials in areas such as environmental monitoring, medical diagnostics, and industrial process control. There are several reasons why researchers are exploring CBFM for optical sensors:

1. Unique properties: The CBFM, such as graphene, CNTs, and CQDs, possess unique optical, electrical, and mechanical properties that make them attractive for developing high-performance optical sensors.
2. High sensitivity and selectivity: The CBFM can detect small changes in the surrounding environment, making them highly sensitive sensors. They can also be engineered to selectively detect specific target analytes, making them highly selective sensors.
3. Biocompatibility: Many CBFM are biocompatible, which makes them suitable for use in biomedical applications such as bioimaging and biosensing.
4. Low cost: The CBFM can be produced in large quantities at a low cost, making them an attractive alternative to other types of sensors that are more expensive and difficult to produce.
5. Environmental applications: The CBFM can be used to detect environmental pollutants, such as heavy metals and organic pollutants, which are harmful to human health and the environment [7].

Finding CBFM for optical sensors has the potential to revolutionize the field of sensing, enabling the development of high-performance, low-cost, and environmentally friendly sensing devices. Some common uses of CBFM for optical sensors are included in Table 1.

The CBFM have unique optical and surface properties, including high absorption and strong fluorescence, which make them promising candidates for optical sensing applications. The surface chemistry and morphology of CBFM can be manipulated to enhance their optical properties, allowing for the selective detection of specific analytes. CBFM has demonstrated sensitivity, selectivity, and stability in detecting gases, chemicals, and biomolecules. They are also biocompatible, non-toxic, and biodegradable, making them suitable for use in biological and medical applications. Overall, CBFM offers a range of advantages as sensing materials due to their unique properties, making them promising materials for future research in optical sensing.

1.1 Properties of Carbon-Based Functional Materials

(a) **Optical Properties**

The unique optical properties of CBFM have made them attractive for optical sensing applications. CBFM possess high absorption coefficients in the ultraviolet to visible light range due to their extended conjugated π-electron systems, which can be utilized to develop photodetectors and optical sensors. CBFM exhibits strong fluorescence emission, which can be exploited to design fluorescence-based optical sensors for

Table 1 Carbon-based material applications in optical sensor technology

Applications	Uses	References
Fluorescence sensing	The CQDs, graphene quantum dots (GQDs), and other carbon-based nanomaterials are used for fluorescence sensing of biomolecules, environmental pollutants, and other substances	[8]
Gas sensing	CNTs, graphene, and other carbon-based nanomaterials are used for optical gas sensing of various gases, such as carbon dioxide, methane, liquefied, and hydrogen	[9]
Environmental monitoring	Carbon-based optical sensors are used for monitoring environmental pollutants, such as heavy metals, organic pollutants, and other contaminants	[10]
Water quality monitoring	Carbon-based optical sensors are used for monitoring the quality of water, such as detecting heavy metals and organic pollutants	
Optical biosensors	Carbon nanotubes, graphene, and other carbon-based nanomaterials are used for optical biosensing of various biomolecules, such as DNA and proteins	[11]
Bioimaging	CQDs, GQDs, and other carbon-based nanomaterials are used for optical bioimaging and disease diagnosis, such as detecting cancer cells and biomarkers	[12]

the detection of various analytes. GQDs have shown remarkable photoluminescence properties and have been used to detect trace amounts of heavy metal ions in water [13]. The fluorescence properties of CBFM can be tuned by controlling their size, shape, and surface functionalization.

(b) **Surface Properties**

The surface chemistry and morphology of CBFM can be manipulated to enhance their optical properties and enable selective detection of specific analytes. CBFM have large surface areas and high surface-to-volume ratios, making their surface properties critical for their sensing performance. Surface functionalization of CBFM can be achieved by introducing various functional groups, such as carboxyl, amino, epoxies, or hydroxyl groups, which can interact with specific analytes and enhance their selectivity [14]. Surface morphology can also be tailored by controlling the size, shape, and aspect ratio of CBFM, which can affect their interaction with analytes and their optical properties. 2D materials, such as graphene and molybdenum disulfide, have shown high sensitivity and selectivity in detecting gas molecules due to their large surface area and unique surface chemistry [15].

(c) **Sensitivity and Selectivity**

Sensitivity and selectivity are important properties of CBFM in optical sensing applications. CBFM has shown high sensitivity and selectivity in detecting various analytes, such as gases, chemicals, and biomolecules. Graphene-based sensors have demonstrated high sensitivity and selectivity in detecting gases such as nitrogen dioxide, ammonia, and hydrogen. The selectivity of graphene-based sensors is due to the specific interactions between the gas molecules and the graphene surface [16]. The sensitivity of CBFM in detecting analytes can be further improved by controlling their surface properties, such as surface functionalization and morphology.

(d) **Biocompatibility and Biodegradability**

The biocompatibility, low toxicity, and biodegradability of CBFM make them suitable for use in biological and medical applications. CBFM has shown biodegradability and can be easily cleared from the body without causing any harmful effects. Graphene oxide has been used for drug delivery and has shown biodegradability and low toxicity in various in vitro and in vivo studies [17]. Moreover, CBFM has been explored for various biomedical applications, including drug delivery, imaging, and sensing. CBFM has low cytotoxicity and can be functionalized with specific biomolecules, such as antibodies, peptides, or DNA, to target specific cells or tissues [18].

Functional materials are essential for sensor applications due to their unique properties and functionalities that allow for the selective detection of specific analytes. Sensors rely on the interaction between the sensing material and the analyte to produce a measurable response. Samiksha et al. [19] used $BaTiO_3$ nanocrystals to create humidity sensors with films deposited on borosilicate glass. The resulting sensors had increased sensitivity with higher ethanol concentrations. Maqsood et al. [20] developed a binder-free ZnO thin film sensor for NH_3 detection and found that gamma-irradiation modified the surface morphology and increased gas response. The researchers investigated how γ-irradiation affects multi-walled CNTs. They discovered that the crystallite size increased and the bandgap decreased due to the formation of charge trapping. The results showed that the nanotubes bunched together and had diameters ranging from 40 to 60 nm. Additionally, the γ-irradiated multi-walled CNTs had an improved structural ordering compared to the pristine ones [21].

Functional materials can be tailored to exhibit specific surface chemistry, morphology, and optical properties, allowing for the sensitive and selective detection of various analytes, including gases, chemicals, and biomolecules. Rakesh et al. [22] fabricated TiO_2-PANI composite films to detect toxic gases. The films showed a diffusion-free interface and porous surface morphology with nanocrystalline grains, which enhanced the sensing response. Researchers emphasize the importance of gas sensors for detecting hazardous pollutants like CO_2, VOCs, NOx, SO_2, and CO in the environment, and hybrid nanomaterials are promising to enhance sensor performance. The MOs-based nanomaterials for detecting dangerous and flammable gases, including the use of noble metals and composites of graphene with MOs. Various methods, including eco-friendly and cost-effective ones, are used for the development of effective sensor devices relies on the use of hybrid nanomaterials [23]. In addition, functional materials can be designed to have high stability, reproducibility, and durability, making them suitable for use in harsh environments or long-term monitoring applications. Therefore, the development of new and advanced functional materials is crucial for the continuous improvement and innovation of sensor technologies. Ongoing research in this field is focused on developing new materials with enhanced sensing properties, improving the sensitivity and selectivity of existing materials, and optimizing the design of optical sensors to maximize their performance.

1.2 Need for Carbon-Based Functional Materials for Optical Sensor Application

Optical sensors are devices that detect changes in light and convert them into electrical signals. These sensors have widespread applications in fields such as environmental monitoring, Water quality monitoring, medical diagnostics, and industrial sensing. However, traditional materials used in optical sensors like ferrite materials [24], silicon, and metal-based materials have certain limitations in terms of sensitivity, stability, and cost. The CBFM has emerged as a promising alternative to overcome these limitations. CBFM possess unique properties such as high sensitivity, stability, and low cost, making them ideal candidates for optical sensor applications. For instance, CNTs are highly sensitive to changes in light and can be functionalized to detect specific molecules or gases. Graphene has high electrical conductivity and can detect changes in light intensity. Additionally, C-dots, which are fluorescent nanoparticles made of carbon, can be used for imaging and sensing applications.

One of the primary advantages of CBFM is their ability to be produced in large quantities and at a low cost, making them an attractive alternative to traditional materials used in optical sensors. Furthermore, they can be integrated with existing sensor platforms, allowing for the development of more sensitive and efficient sensors. CBFM also has the potential to enable new applications in optical sensing. They could be used to develop sensors for real-time monitoring of air quality, detecting contaminants in water, or diagnosing diseases in a patient's blood. The use of CBFM in optical sensors could lead to more accurate and reliable detection of various substances and provide valuable insights into the environment and human health. The need for CBFM in optical sensor applications arises from the limitations of traditional materials and their unique properties such as high sensitivity, stability, and low cost. With their potential to enable new applications and improve the performance of existing sensors, CBFM represents a promising avenue for the future of optical sensing.

1.3 The Carbon-Based Functional Materials: Useful Synthesis Methods, Carbon Nanostructures and Doping Effects

(a) **Synthesis Methods**

Each technique has its own unique advantages and disadvantages depending on the desired properties and applications of the carbon-based nanomaterial, includes:

- Precise control over the size, shape, and structure of the nanomaterials.
- High purity and reproducibility.
- Scalability for mass production.
- Ability to functionalize the surface of the nanomaterials for specific applications.
- Low-cost and energy-efficient synthesis.

Chemical Vapor Deposition is widely used for producing high-quality graphene and CNTs, while arc discharge is suitable for producing CNTs with a high aspect ratio. Hydrothermal/solvothermal synthesis is a versatile technique for producing a wide range of carbon-based nanomaterials, and electrochemical synthesis offers a green and sustainable approach to nanomaterial synthesis. Overall, the choice of synthesis technique depends on the specific application and desired properties of the carbon-based functional nanomaterials.

(b) **Carbon Nanostructures**

The choice of carbon nanostructure for optical sensing devices depends on the specific application and required properties.

- CNTs are known for their high sensitivity to changes in light and can be functionalized to detect specific molecules or gases.
- Graphene has high electrical conductivity and can detect changes in light intensity, making it useful for photodetectors and optical modulators.
- C-dots are fluorescent nanoparticles made of carbon and can be used for imaging and sensing applications, including biomedical sensing.
- Doping of carbon nanostructures with other elements, such as nitrogen or sulfur, can enhance their optical sensing performance, including sensitivity, selectivity, and stability.
- Hybrid carbon nanostructures, such as carbon nanotube-graphene composites, can combine the unique properties of different carbon nanostructures to improve sensing performance.

(c) **Doping Effects**

Doping CBFM with other elements, such as nitrogen or sulfur, can improve the optical sensing performance of the sensor in several ways. These include:

- Enhanced sensitivity: Doping can increase the sensitivity of the carbon nanomaterial to changes in light or other stimuli, improving the detection limit and accuracy of the sensor.
- Tunable selectivity: Doping can modify the chemical properties of the carbon nanomaterial, allowing for selective detection of specific molecules or gases. This can improve the specificity and selectivity of the sensor.
- Improved stability: Doping can enhance the stability and durability of the carbon nanomaterial, making it more resistant to degradation or chemical reactions. This can improve the longevity and reliability of the sensor [25].

The specific effects of doping on optical sensing performance depend on factors such as the type and concentration of dopant used, as well as the characteristics of the carbon nanomaterial being doped. Nonetheless, doping is generally considered a useful strategy for optimizing the optical sensing performance of CBFM.

1.4 Overview of Carbon-Based Functional Materials

The CBFM, such as graphene, carbon nanotubes, and carbon dots, have unique properties that make them attractive for various applications, including optical sensors. These materials possess high surface area, excellent electrical and optical properties, and can be easily functionalized for specific applications. Table 2 provides information on carbon-based materials used for optical sensing applications.

The research and development of CBFM for optical sensing applications is a global endeavor, with contributions from many countries around the world. Here are some examples of research activities in different regions:

Table 2 Carbon-based materials including graphene, carbon nanotubes, carbon dots, diamond, and carbon fibers studied for optical sensing applications

Materials	Explanation	References
Graphene	A two-dimensional carbon material that consists of a single layer of carbon atoms arranged in a hexagonal lattice. Graphene has excellent optical properties, including high transparency and strong light-matter interactions, making it a promising material for optical sensors	[26]
Carbon nanotubes	Cylindrical structures made up of carbon atoms have a high aspect ratio and unique electronic and optical properties. CNTs used as optical sensors by exploiting their optical absorbance or luminescence properties	[27]
Carbon dots	Carbon nanoparticles in a size range of 1–10 nm exhibit strong photoluminescence. C-dots have been used as optical sensors due to their strong fluorescence signal and ability to interact with analytes through surface functionalization	[28]
Diamond	A form of carbon that has a diamond crystal lattice structure and is transparent in the visible and ultraviolet regions of the electromagnetic spectrum. It is used as an optical sensor by exploiting its ability to interact with analytes through surface functionalization or by detecting changes in its optical properties due to strain or defects	[29]
Carbon fibers	Long, thin strands of carbon with a high aspect ratio exhibit high mechanical strength and thermal conductivity. It is used as an optical sensors by exploiting their ability to interact with analytes through surface functionalization or by detecting changes in their optical properties due to mechanical deformation	[30]

- **North America**

a. In the United States, several research institutions and universities have been active in developing CBFM for optical sensors. For example, researchers at the University of Houston, Janire [31], have developed a graphene-based biosensor for the detection of DNA, while researchers at the University of Pittsburgh and The National Energy Technology Laboratory, have used CNTs as sensing elements in gas sensors [32].
b. Researchers from the United States, Massachusetts Institute of Technology, developed a diamond-based biosensor for time-resolved magnetic sensing with electronic spins to monitor intracellular processes [33].

- **Europe**

a. In Europe, many research groups have been exploring the use of carbon-based materials for optical sensing. For instance, researchers at the University of Manchester in the UK have been studying the use of graphene as a wearable sensing material in textile [34], while researchers at the Department of Biosystems Science and Engineering in ETH Zurich, have developed a carbon nanotube-based sensor for the detection of neurotransmitter glutamate [35].
b. Researchers from Palacký University Olomouc presented a graphene-based optical biosensor for the detection of SARS-CoV-2 antibodies [36].

- **Asia**

a. In Asia, there has been significant research and development of CBFM for optical sensing. For example, researchers at Biomedical Engineering Academy in China have developed a graphene oxide-based sensor for the detection of glucose [37], while researchers at the National University of Singapore have used C-dots as fluorescent probes for the detection of metal ions [38].

- **Oceania**

a. Researchers from Australia developed a carbon-based biosensor for clinical diagnosis to detection of cancer and disease biomarkers [39].

These examples demonstrate the global interest and investment in CBFM for optical sensor applications, with researchers from different regions exploring their potential in a wide range of sensing applications. The ongoing research in this field is expected to lead to even more advanced and practical optical sensor technologies in the future. There has been significant recent research on CBFM for optical sensor applications. Here are a few examples:

1. Graphene-based optical sensors: Xiao-guang gao et al. [40] presented graphene and its derivatives-based optical sensors.
2. C-dots for heavy metal ion sensing: Simei et al. [41] presented a carbon dot-based sensor for the detection of heavy metal ions.
3. Carbon nanotube-based gas sensors: Twinkle et al. [42] presented a recent development of graphene and CNTs-based gas sensors.
4. Diamond-based biosensors: Nádia et al. [43] presented a diamond-based biosensor for detecting molecules, such as DNA and proteins.
5. Carbon fiber-based sensors: Alexander Horoschenkoff and Christian Christner [44] presented a carbon fiber-based sensor for the detection of stress analysis, damage detection, and the monitoring of manufacturing processes.

The interaction between CBFM and analytes can result in changes in their optical properties, such as absorption, fluorescence, and reflection, which can be detected by optical sensors. By monitoring these changes, optical sensors can provide highly sensitive and selective detection of analytes in real-time. Overall, CBFM offers promising opportunities for the development of highly sensitive and selective optical sensors. Ongoing research in this field is focused on improving the performance of these materials, optimizing the design of optical sensors, and developing new materials with enhanced sensing properties. These recent studies highlight the potential of CBFM for optical sensor applications, including biosensing, environmental monitoring, and chemical sensing.

1.5 Optical Sensing

Optical sensing is a non-destructive analytical technique that measures changes in the optical properties of a material in response to the presence of an analyte. Optical sensors have gained significant attention due to their high sensitivity, selectivity, and real-time detection capabilities. Optical sensors are used in various applications, including healthcare, environmental monitoring, and industrial process control.

An optical sensor is an electronic device that detects and measures changes in light intensity, color, or polarization. Optical sensors work on the principle of transduction, which converts an input quantity, such as light intensity or color, into an electrical signal. The basic components of the optical sensor shown in Fig. 2 include a light source, a sensing element, a detector, and a signal processing circuit. The light source emits light, which is then directed to the sensing element. The sensing element interacts with the light and produces a response, which is detected by the detector. The detector converts the response into an electrical signal, which is then processed by the signal processing circuit. The most commonly used sensing elements in optical sensors are photodiodes and phototransistors. Photodiodes are semiconductor devices that convert light into an electrical current. Phototransistors are similar to photodiodes, but they have a third electrode, which allows them to amplify the electrical signal.

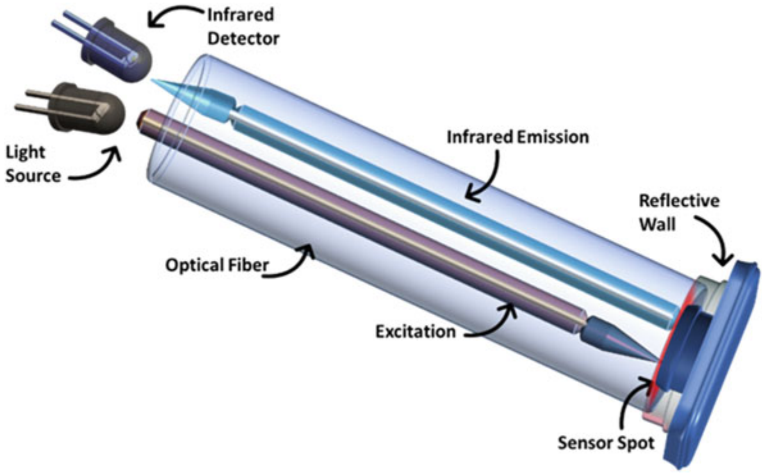

Fig. 2 The basic components and working principle of an optical sensor, which converts light into an electrical signal for various applications. © Sohel Shaikh, (2023) All rights reserved

There are several different types of optical sensors, each of which works on a slightly different principle. Some of the most used types of optical sensors include:

1. Photoelectric sensors: These sensors work by emitting a beam of light toward an object and detecting the amount of light that is reflected back. They are commonly used for detecting the presence of objects, measuring distances, and detecting motion.
2. Fiber optic sensors: These sensors use a fiber optic cable to transmit light to and from the sensing element. They are used for measuring temperature, pressure, and strain.
3. Spectroscopic sensors: These sensors use the principles of spectroscopy to detect and measure the chemical composition of a sample. They are commonly used in chemical analysis and environmental monitoring.
4. Image sensors: These sensors are used to capture images using an array of photodiodes or phototransistors. These are commonly used in digital cameras, scanners, and other imaging devices.

Table 3 provides information on CBFM used in optical sensors and their applications. It lists various targeted molecules, such as glucose, DNA, proteins, iron ions, and levodopa, and their corresponding carbon-based materials, including graphene oxide, graphene, single-walled CNTs, CQDs, and C-dots. The sensors use different methods such as fluorescent and electrochemical detection and have different ranges and LOD. The findings of the studies include the detection of glucose, typhoid, heavy metal ions, and levodopa in various environments, such as water and human serum, with high accuracy and sensitivity. These carbon-based materials show promising potential for environmental and biological sensing applications.

Table 3 The use of CBFM in optical sensors and their related applications

Sr. no.	Targeted molecules	Materials	Method	Range	Findings	References
1	Glucose	Graphene oxide	Fluorescent	2–75 mg/L	Detects the glucose in water of 7.4 pH	[45]
2	Glucose	Graphene	Electrochemical	0–6 mM	The sensitivity of glucose detection is 1.63 mA mM^{-1} cm^{-2} and the stability is 76.9% after one month	[45]
3	DNA	Graphene oxide	Electrochemical	10 fM to 50 nM	The detection limit for typhoid is 100 fM at 25 °C	[46]
4	Proteins	Graphene oxide	Fluorescent	0.1–5.0 U mL^{-1}	The detection limit for H-89 on protein kinase activity in cell lysates is at 0.039 U/mL	[47]
5	Glucose	Single-walled CNTs	Electrochemical	0.5–50 μM	The sensitivity of 135.9 μA mM^{-1} for glucose at a LOD of 0.1 μM	[48]
6	Iron ion and ascorbic acid	CQDs	Fluorescent	0–300 μmol L^{-1}	Detects different metal ions for environmental and biological sensing at LOD 13.68 μmol L^{-1}	[49]
7	Hg^{2+} and biothiols	Carbon dots	Fluorescent	0.05–10 μM	Detects Hg^{2+} ions in water and biothiols samples in human plasma at LOD 44 nM	[50]
8	Iron ions	CQDs	Fluorescent	0–150 μM	The quantitative detection of heavy metal ions in aqueous environment at LOD 0.24 μM	[51]

(continued)

Table 3 (continued)

Sr. no.	Targeted molecules	Materials	Method	Range	Findings	References
9	Fe^{3+} and fluoroquinolones detection	CQDs	Fluorescent	0–1300 nM	Sensor detects more than one analyte. The ofloxacin and ciprofloxacin with selectivity and sensitivity of 150 nM and 127 nM, respectively	[52]
10	Levodopa	CQDs	Fluorescent	0.05–1 μM	Levodopa in human serum monitoring with accuracy at LOD 0.057 μM	[53]

Overall, optical sensors are versatile devices that can be used in a wide range of applications. Their ability to detect changes in light intensity, color, and polarization makes them particularly useful for sensing and monitoring applications.

2 Graphene-Based Optical Sensors

2.1 Introduction to Graphene

Graphene is a two-dimensional carbon material with high surface area and excellent electrical and optical properties. Graphene-based optical sensors (GBOS) are demonstrated for the detection of various gases, liquids, and biomolecules. In this section, we will explore the potential of graphene for optical sensing applications.

Graphene was first isolated and characterized by Andre Geim and Konstantin Novoselov at the University of Manchester in 2004, and they were awarded the Nobel Prize in Physics in 2010 for their work on graphene [54]. Since then, graphene has generated enormous interest due to its unique combination of properties, including its high electrical conductivity, thermal conductivity, and mechanical strength. Graphene has shown great promise in optical sensing applications due to its unique optical properties, including its high surface area, transparency, and sensitivity to changes in the local refractive index. One common approach to utilizing graphene in optical sensors is by using it as a surface-enhanced Raman spectroscopy (SERS) substrate. SERS is a technique that can detect trace amounts of molecules using a laser to excite them on a metal surface, which enhances their Raman scattering signal. Figure 3a is a graphene-based SERS sensor, which enhances the Raman scattering signal of a target molecule by functionalizing the graphene layer with specific molecules that bind to the analyte. This enables the sensor to detect various analytes with high sensitivity and selectivity [55]. Figure 3b is a graphene-based Ferromagnetic Resonance Tunneling (FERT) sensor, The FERT sensor is made up of a ferromagnetic layer sandwiched between two graphene layers. When a magnetic field is close to the sensor, it changes the electrical resistance of the sensor. To measure the amount of light emitted from a sample, a photoluminescence (PL) detector is used. This detector collects the photons of light emitted from the sample and converts them into an electrical signal. By detecting the change in electrical resistance caused by the magnetic field, the FERT sensor determines the presence and strength of the field [56]. Because of its design, the FERT sensor has high sensitivity and fast response times, making it well-suited for applications that require quick and accurate detection of magnetic fields. Examples of such applications include magnetic field sensing and magnetic data storage.

Another way graphene can be used in optical sensors is by utilizing its optical absorption properties. Graphene has a unique absorption spectrum that changes with the surrounding environment, making it sensitive to changes in the local refractive index. This sensitivity can be exploited to detect analytes in solution or

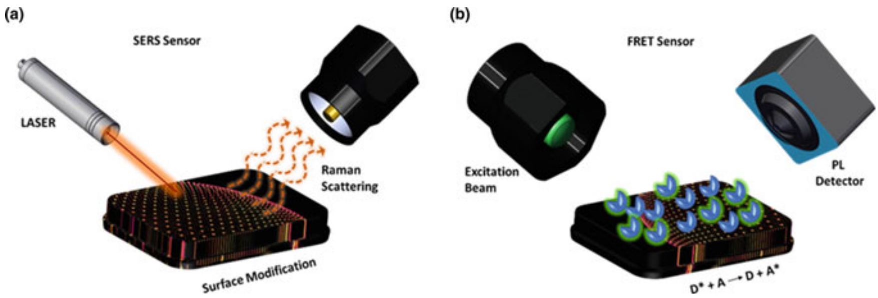

Fig. 3 **a**, **b** Depicting the use of graphene material in the development of optical sensors for high sensitivity and selective detection of various analytes.

gas phase. Additionally, graphene can be integrated with other materials to create composite materials that exhibit enhanced optical properties. For example, graphene can be combined with plasmonic nanoparticles to create hybrid materials that exhibit enhanced SERS and photothermal effects [26, 57].

Overall, graphene has shown great potential for use in optical sensing applications due to its unique optical properties and the ability to integrate it with other materials to create hybrid materials with enhanced properties. However, more research is needed to optimize the synthesis and processing of graphene-based materials for use in practical optical sensing applications.

2.2 *Graphene-Based Optical Sensor Fabrication*

Various techniques have been developed for the fabrication of graphene-based optical sensors, including surface plasmon resonance (SPR), optical absorption, and Raman spectroscopy. In this section, we will explore the different fabrication techniques for graphene-based optical sensors.

Figure 4 shows the use of graphene material in SPR-based optical sensors. The biomolecules of interest are immobilized on the surface of the graphene, and when the analyte molecules bind to the biomolecules, they cause changes in the refractive index of the surrounding medium. These changes in the SPR signal can be detected in real-time, enabling highly sensitive detection of the analytes. Graphene's unique properties, such as high surface area, electron mobility, and strong plasmonic resonance, make it an ideal material for SPR-based optical sensors with potential applications in various fields [58].

There are several methods for fabricating GBOS, which include:

1. Chemical Vapor Deposition (CVD): In this method, a thin film of graphene is grown on a substrate by exposing it to a carbon-containing gas under high temperature and pressure. The resulting graphene film can then be transferred onto a target substrate, such as a glass slide, and used for optical sensing applications.

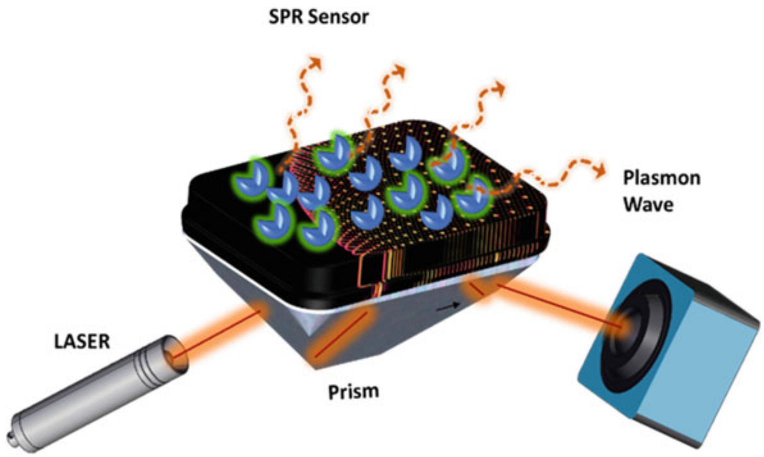

Fig. 4 Use of graphene material in SPR-based optical sensors for highly sensitive detection of biomolecules and other analytes in real-time. © Sohel Shaikh, (2023) All rights reserved

2. Transfer Method: Graphene can be transferred onto a target substrate from a donor substrate using various transfer methods, such as dry transfer, wet transfer, or stamp transfer. This method is commonly used to transfer large-area graphene films onto flexible substrates or onto patterned substrates for device fabrication.
3. Solution-Based Methods: Graphene oxide can be synthesized using Hummer's method or other oxidation methods and then reduced to obtain reduced graphene oxide (rGO). The rGO can be dispersed in solution and then deposited onto a substrate using techniques, such as spin coating, spray coating, or inkjet printing. These methods are commonly used to fabricate graphene-based sensors on flexible substrates.
4. Lithography: Graphene can be patterned using lithographic techniques, such as electron beam lithography or photolithography, to create micro- and nanostructures that can be used for optical sensing applications.

Once the graphene film or pattern is deposited onto a substrate, the surface can be functionalized to enhance optical adsorption, molecular adsorption, thermo-optic, surface plasmon, photoluminescence, etc. properties to promote highly sensitive results. This can be achieved by modifying the surface chemistry of the graphene through various chemical treatments, such as oxidation or functionalization with chemical groups that can interact with the target analyte [59, 60].

Finally, the optical sensing performance of the GBOS can be characterized using various techniques, such as Raman spectroscopy or absorption spectroscopy, to measure the response of the graphene to changes in the local environment. Once the GBOS is fabricated and characterized, it can be integrated into a complete sensing system. This may involve incorporating the sensor into a microfluidic device, which allows the target analyte to flow over the surface of the sensor, increasing the sensitivity of the detection. The device can also include a light source and detector for measuring the changes in optical properties of the graphene as the target analyte interacts with it.

One advantage of using GBOS is their potential for high sensitivity and selectivity. The unique optical properties of graphene, combined with its high surface area, make it a highly sensitive material for detecting changes in the local environment. Additionally, functionalizing the graphene surface can further enhance the selectivity of the sensor for specific analytes. GBOS also has the potential for real-time monitoring and remote sensing applications. The sensor response can be monitored in real-time using a microfluidic device or other sensing system, allowing for continuous monitoring of the target analyte. Additionally, GBOS can be integrated into wireless or remote sensing systems, enabling remote monitoring of the target analyte [61].

In conclusion, the fabrication of GBOS involves depositing graphene onto a substrate, functionalizing the surface, and characterizing its optical sensing properties. These sensors have the potential for high sensitivity and selectivity and can be integrated into microfluidic devices or remote sensing systems for real-time monitoring and remote sensing applications.

2.3 Graphene-Based Optical Sensor Applications

The GBOS have been used for the detection of glucose, dopamine, and hydrogen peroxide with high sensitivity and selectivity. In this section, we will explore the different applications of GBOS.

Figure 5 shows the versatility of graphene in sensing applications, as it enables rapid and sensitive detection of various substances, such as gases, proteins, and DNA, among others. The colorimetric approach used in these sensors allows for easy and rapid detection, making them suitable for various applications, including environmental monitoring and medical diagnostics. The graphene-based sensing platform can produce color changes upon exposure to the target analytes, making it a promising tool for rapid and easy detection of various molecules, such as gases, biomolecules, and chemicals. The GBOS are also highly sensitive and can detect analytes at low concentrations, making them useful for a wide range of applications in environmental monitoring, medical diagnostics, and food safety. The use of graphene in colorimetric optical sensors holds great promise for advancing the field of analytical chemistry and sensor technology.

The GBOS have a wide range of potential applications, including;

1. Environmental Monitoring: The GBOS can be used to detect pollutants and toxins in the environment, such as heavy metals, organic pollutants, and harmful gases. For example, graphene-based sensors have been used to detect nitrogen dioxide, a common air pollutant [62].
2. Food and Agriculture: The GBOS can be used to detect contaminants in food and water, such as pesticides and bacteria. This can help ensure food safety and prevent foodborne illnesses [63].

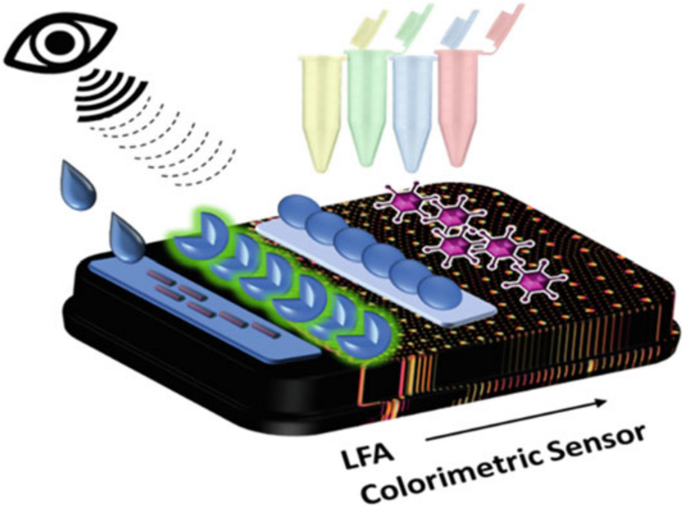

Fig. 5 Use of graphene material in colorimetric optical sensors for rapid and sensitive detection of various analytes through color changes in the graphene-based sensing platform. © Sohel Shaikh, (2023) All rights reserved

3. Biomedical Applications: The GBOS can be used for various biomedical applications, such as detecting biomolecules and monitoring drug delivery. For example, graphene-based sensors have been used for human health monitoring [64].
4. Industrial Applications: The GBOS can be used in industrial applications, such as detecting leaks in pipelines and monitoring the quality of industrial gases. For example, graphene-based sensors have been used to detect vapor of volatile organic compounds, NO_2, H_2, SO_2, CO, H_2S, NH_3, and gas leakages in oil and gas pipelines [65].
5. Defence and Security: The GBOS can be used for various defence and security applications, such as detecting explosives and chemical warfare agents. For example, graphene-based sensors have been used to detect trace amounts of Trinitrotoluene, a common explosive [66].

Overall, GBOS have the potential to revolutionize sensing applications in various industries and fields, due to their high sensitivity and selectivity, real-time monitoring capabilities, and potential for remote sensing. However, further research is needed to optimize the fabrication and functionalization of GBOS for specific applications and to overcome any potential limitations or challenges.

3 Carbon Nanotube-Based Optical Sensors

3.1 Introduction to Carbon Nanotubes

The CNTs are another type of carbon-based material that has been explored for optical sensing applications. CNTs have high aspect ratio, large surface area, and excellent mechanical and electrical properties. In this section, we will explore the potential of CNTs for optical sensing applications.

The CNTs are a unique form of carbon allotrope that has received significant attention due to their remarkable physical, mechanical, and electrical properties. Figure 6 shows the application of CNTs in optical sensors to achieve high sensitivity and selective detection of a range of analytes such as gases, biomolecules, and chemicals. The CNTs are used as sensing elements, which interact with the analyte and produce a measurable response. These sensors are highly sensitive due to the unique properties of carbon nanotubes, such as their high surface area and strong interaction with the analyte. They are essentially cylindrical tubes made up of carbon atoms arranged in a hexagonal lattice pattern. The CNTs can be single-walled or multi-walled, with the former having a diameter of just a few nanometers and the latter consisting of several concentric tubes with increasing diameters. The CNTs are incredibly strong, lightweight, and have high thermal and electrical conductivity. They also exhibit unique optical properties and can be either metallic or semiconducting, depending on their structure. Because of these properties, CNTs have a wide range of potential applications, such as in electronics, energy storage, and nanocomposites.

The discovery of CNTs is credited to Japanese physicist Sumio Iijima in 1991, and since then, researchers have made significant progress in understanding their properties and potential applications. However, challenges still exist in producing large quantities of high-quality CNTs and integrating them into practical devices.

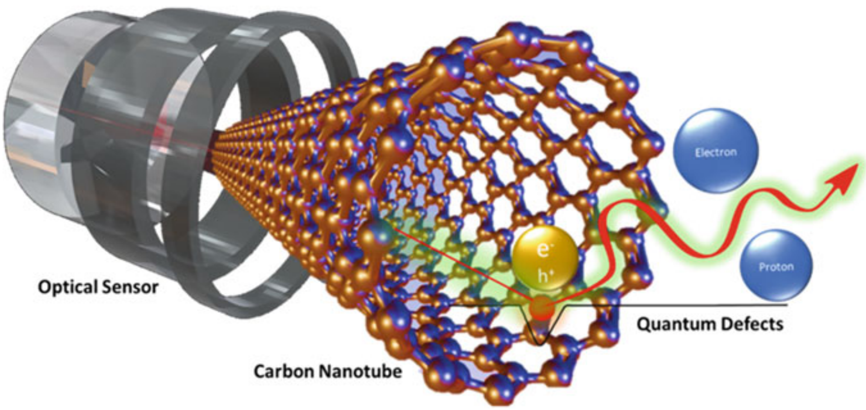

Fig. 6 The use of CNTs in optical sensors for high sensitivity and selective detection of various analytes, including gases, biomolecules, and chemicals.

Nonetheless, the unique properties of CNTs continue to make them an area of active research and development in materials science and nanotechnology [67].

The CNTs have emerged as a promising material for optical sensors due to their unique optical properties. The CNTs have a high aspect ratio, which means that they have a large surface area-to-volume ratio. This property allows CNTs to interact strongly with light, making them an ideal candidate for optical sensing applications. One of the most significant advantages of using CNTs in optical sensors is their ability to absorb and emit light in the near-infrared (NIR) range. The NIR region is of great interest for sensing applications because it is biologically safe, meaning that it does not cause any harmful effects on living cells. Additionally, many biomolecules, such as glucose and hemoglobin, have characteristic absorption and scattering properties in the NIR range, making it an ideal region for sensing applications.

Another advantage of CNTs in optical sensors is their ability to act as a transducer. CNTs can convert optical signals into electrical signals, enabling them to be easily integrated into electronic circuits for readout and signal processing. This property makes CNTs a versatile material for optical sensing applications, as they can be used for both detection and signal transduction. Finally, CNTs also have a high sensitivity to small changes in their environment, such as changes in temperature, pressure, and chemical composition. This property makes them an ideal candidate for sensing applications, where they can be used to detect small changes in their environment and provide a sensitive and accurate measurement of the target analyte [68].

Overall, the unique optical properties of CNTs make them a promising material for optical sensing applications, particularly in the NIR range. Their high sensitivity, transducing ability, and ability to interact strongly with light make them versatile materials for a wide range of sensing applications, including biomedical sensing, environmental monitoring, and chemical sensing.

3.2 Carbon Nanotube-Based Optical Sensor Fabrication

Various techniques have been developed for the fabrication of Carbon Nanotube-Based Optical Sensor (CNT-BOS), including SPR, optical absorption, and fluorescence spectroscopy. In this section, we will explore the different fabrication techniques for CNT-BOS.

Fabrication of CNT-BOS involves several steps, including CNT synthesis, CNT dispersion, substrate preparation, and device assembly. Here is a brief overview of the steps involved in the fabrication of CNT-BOS:

1. CNTs Synthesis: CNTs can be synthesized using various methods, including CVD, arc discharge, and laser ablation. The synthesis method used will depend on the desired properties of the CNTs and the intended application.

2. CNTs Dispersion: CNTs are typically synthesized in the form of aggregates or bundles, which must be dispersed to create a uniform solution. The dispersion process involves adding a surfactant or dispersant to the CNTs and sonicating the mixture to break up the aggregates.
3. Substrate Preparation: The substrate is typically a glass or silicon wafer, which is cleaned and coated with a thin layer of metal, such as gold or silver, to enhance the sensitivity of the sensor.
4. Device Assembly: The CNTs dispersion is then drop-casted onto the substrate and dried to create a uniform CNTs film. The CNTs film is then coated with a layer of polymer, such as polyvinyl alcohol, to improve its stability and adhesion to the substrate.
5. Sensing Mechanism: The sensing mechanism depends on the application and can be based on changes in the CNTs film's electrical conductivity, optical properties, or mechanical properties.

For optical sensing applications, the CNTs film is typically used as a transducer to convert the optical signal into an electrical signal. The CNTs film absorbs light in the NIR range, and any changes in the surrounding environment, such as changes in the refractive index or absorption, will cause a change in the CNTs film's optical properties, leading to a change in the electrical conductivity. This change in conductivity can be measured using electrodes placed on either side of the CNTs film, and the signal can be processed to obtain information about the target analyte [69].

In summary, the fabrication of CNT-BOS involves synthesizing and dispersing CNTs, preparing the substrate, assembling the device, and determining the sensing mechanism. The unique properties of CNTs make them a promising material for optical sensing applications, particularly in the NIR range.

3.3 Carbon Nanotube-Based Optical Sensor Applications

CNT-BOS has been used for the detection of glucose, DNA, and proteins with high sensitivity and selectivity. In this section, we will explore the different applications of CNT-BOS.

The potential of CNT-BOS in various fields is shown in Fig. 7, where accurate and reliable detection of analytes is essential. CNT-BOS has emerged as a promising technology due to their unique properties such as high sensitivity, selectivity, and fast response time. These sensors can be used to detect and monitor pollutants in the air, water, and soil in environmental monitoring. In medical diagnostics, they can be used for the detection of biomarkers and diseases. In industrial sensing, they can be used for process control and monitoring of chemical reactions.

Here are some examples of the applications of CNT-BOS:

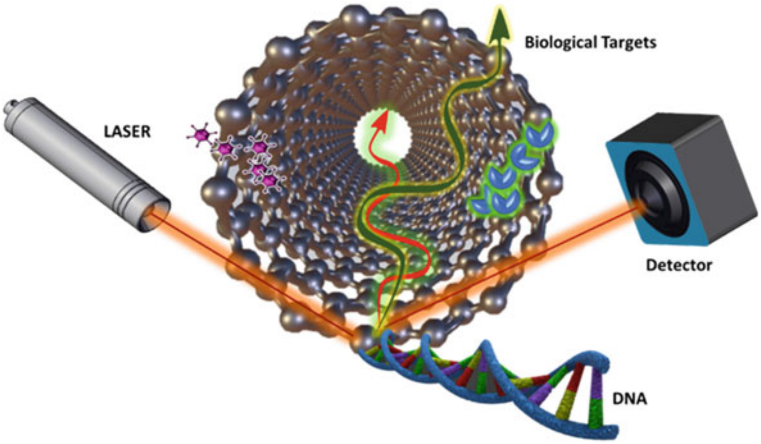

Fig. 7 Diverse range of applications for carbon nanotube-based optical sensors, including environmental monitoring, medical diagnostics, and industrial sensing.

1. Biomedical Sensing: CNT-BOS has the potential to revolutionize biomedical sensing by providing non-invasive, real-time, and high-sensitivity measurements of biomolecules in the body. For example, CNT-based sensors can be used to detect glucose, hemoglobin, and other biomolecules in the NIR range, which is biologically safe and does not cause any harmful effects on living cells. This makes them ideal for applications such as continuous glucose monitoring for diabetes patients [70].
2. Environmental Monitoring: CNT-BOS can be used for environmental monitoring by detecting and quantifying pollutants in the air, water, and soil. For example, CNT-BOS can be used to detect heavy metals, pesticides, and other pollutants in water, providing a sensitive and accurate measurement of the target analyte [71].
3. Chemical Sensing: CNT-BOS can be used for chemical sensing by detecting and quantifying gases and vapors in the environment. For example, CNT-BOS can be used to detect carbon dioxide, ammonia, and other gases, providing a sensitive and accurate measurement of the target analyte [72].
4. Structural Health Monitoring: CNT-BOS can be used for structural health monitoring by detecting and quantifying strain and deformation in materials such as concrete, composites, and metals. For example, CNT-based sensors can be embedded in concrete structures to monitor the structural health of the building and detect any changes that may indicate damage or deterioration [73].

Overall, CNT-BOS has the potential to revolutionize sensing applications by providing high sensitivity, real-time, and non-invasive measurements of a wide range of analytes. Their unique optical properties, including their ability to absorb and emit light in the NIR range, make them an ideal candidate for a wide range of applications, including biomedical sensing, environmental monitoring, chemical sensing, and structural health monitoring.

4 Carbon Dot-Based Optical Sensors

4.1 Introduction to Carbon Dots

The C-dots are fluorescent carbon nanoparticles with high quantum yield, stability, and biocompatibility. In this section, we will explore the potential of C-dots for optical sensing applications.

C-dots are a class of carbon-based nanomaterials that are emerging as a promising alternative to traditional quantum dots in various applications. C-dots are typically less than 10 nm in size and consist of a carbon core surrounded by surface functional groups such as hydroxyl, carboxyl, and amino groups. The surface functional groups are responsible for the unique optical, electronic, and chemical properties of C-dots. C-dots can be synthesized using various methods, including hydrothermal synthesis, microwave synthesis, and electrochemical synthesis. The synthesis method used will depend on the desired properties of the C-dots and the intended application. C-dots can be easily functionalized with various surface functional groups to modify their properties, such as their optical properties, solubility, and biocompatibility. C-dots exhibit unique optical properties such as strong fluorescence, photostability, and tunable emission, which make them attractive for various applications such as bioimaging, sensing, and optoelectronics. Additionally, C-dots are biocompatible, non-toxic, and have a low environmental impact, making them ideal for biological and environmental applications. Overall, C-dots are a promising class of carbon-based nanomaterials that offer unique optical and chemical properties and have the potential to revolutionize various fields, including bioimaging, energy storage, sensing, and optoelectronics [74].

C-dots have unique properties that make them promising candidates for optical sensor applications. Their fluorescence properties, high sensitivity, selective sensing, biocompatibility, and environmental stability make them an attractive option for various sensing applications. Ongoing research in this field is expected to further enhance our understanding of their properties and potential applications in optical sensing.

4.2 Carbon Dots-Based Optical Sensor Fabrication

Various techniques have been developed for the fabrication of carbon dots-based optical sensors (C-dots-BOS), including fluorescence spectroscopy. In this section, we will explore the different fabrication techniques for C-dots-BOS.

The fabrication of C-dots-BOS typically involves the following steps;

1. Synthesis of carbon dots: C-dots can be synthesized using various methods, including microwave-assisted synthesis, hydrothermal synthesis, and electrochemical synthesis. The synthesis method used can affect the properties of the C-dots, such as their size, shape, and surface functionalization.
2. Surface functionalization: The surface of C-dots can be functionalized with various functional groups, such as carboxyl, amine, and hydroxyl groups, to tailor their properties for specific applications. Surface functionalization can be achieved using various methods, including covalent functionalization, electrostatic adsorption, and ligand exchange.
3. Sensor material preparation: The C-dots are typically incorporated into a sensing material, such as a polymer matrix, to form a composite material that can be used for sensing applications. The sensing material can be prepared using various methods, including spin coating, drop casting, and inkjet printing.
4. Sensor device fabrication: The composite material is then fabricated into a sensor device, such as a thin film or a micro/nanostructure, for optical sensing applications. The device fabrication method can vary depending on the specific application and can involve techniques such as photolithography, etching, and deposition.
5. Sensor testing and characterization: The fabricated sensor device is then tested and characterized for its sensing performance, including sensitivity, selectivity, response time, and stability. The testing can be carried out using various methods, including spectroscopy, microscopy, and electrochemistry [75].

The fabrication of C-dots-BOS involves synthesizing carbon dots, functionalizing their surface, preparing a sensing material, fabricating a sensor device, and testing and characterizing the sensor performance. The specific methods used for each step can vary depending on the desired properties and applications of the sensor.

4.3 Carbon Dots-Based Optical Sensor Applications

C-dots-BOS have been used for the detection of glucose, dopamine, and proteins with high sensitivity and selectivity. In this section, we will explore the different applications of C-dots-BOS.

C-dots are nanoscale carbon particles with unique optical properties that can be used as sensing elements in optical sensors. Figure 8 shows the broad range of applications for C-dots-BOS. These sensors can be used for the detection of heavy

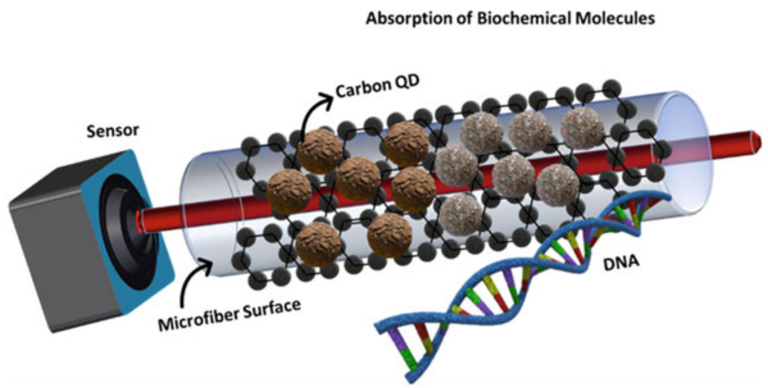

Fig. 8 The broad range of applications for carbon dots-based optical sensors, including sensing of heavy metals, gases, and bioanalytes, as well as imaging and bioimaging applications.

metals, gases, and bioanalytes with high sensitivity and selectivity. C-dots-BOS can also be used in imaging and bioimaging applications. The versatility and potential of carbon dots-based optical sensors make them a promising technology for a wide range of applications in various fields such as environmental, biomedical, health, and industrial sensing.

Here are some of the common applications of C-dots-BOS:

1. Environmental sensing: C-dots-BOS have been used for environmental sensing applications, such as the detection of heavy metal ions, pollutants, and toxic gases. C-dots can be functionalized with specific surface groups to selectively detect target analytes in environmental samples [76].
2. Biomedical sensing: C-dots-BOS have been explored for various biomedical sensing applications, such as the detection of biomolecules, proteins, and cells. C-dots can be functionalized with specific surface groups to selectively interact with target biomolecules or cells, making them useful for medical diagnosis and drug discovery [77].
3. Food safety monitoring: C-dots-BOS have been used for food safety monitoring applications, such as the detection of foodborne pathogens and contaminants. C-dots can be functionalized with specific surface groups to selectively detect target analytes in food samples [78].
4. Chemical sensing: C-dots-BOS have been used for chemical sensing applications, such as the detection of explosives and volatile organic compounds (VOCs). C-dots can be functionalized with specific surface groups to selectively detect target analytes in chemical samples [79].
5. Structural health monitoring: C-dots-BOS have been used for structural health monitoring applications, such as the detection of strain, temperature, and pressure. C-dots can be embedded into structural materials to form optical sensing layers that can monitor changes in the structure [80].

C-dots-BOS have potential applications in various fields, including environmental monitoring, biomedical sensing, food safety monitoring, chemical sensing, and structural health monitoring. Ongoing research in this field is expected to further enhance our understanding of the properties and potential applications of C-dots-BOS, leading to new and exciting opportunities for their use in optical sensing.

5 Advantages, Disadvantages, and Future Directions

5.1 Advantages and Disadvantages

Despite the significant progress in the development of CBFM for optical sensing applications, there are still advantages and disadvantages that need to be addressed including scalability, stability, reproducibility, and sensitivity.

The CBFM offers the following advantages and disadvantages for optical sensor applications.

- **Advantages**

1. High sensitivity: CBFM such as graphene and CNTs exhibit high surface-to-volume ratios and strong light-matter interactions, making them highly sensitive to changes in their environment.
2. Tunable properties: CBFM can be tailored to exhibit specific properties, such as optical absorbance or luminescence, through surface functionalization or by controlling their size and shape.
3. Low cost: CBFM are abundant and relatively low cost compared to other materials used in optical sensing, such as noble metals or semiconductors.
4. Biocompatibility: Some CBFM, such as CNTs and graphene, have shown good biocompatibility and low toxicity, making them suitable for biological and medical applications.
5. Stability: CBFM is generally stable and can withstand a wide range of environmental conditions, including high temperature, pressure, and humidity.

- **Disadvantages**

1. Limited selectivity: CBFM may exhibit limited selectivity for specific analytes, which can result in false-positive or false-negative readings.
2. Interference: The optical properties of CBFM can be affected by environmental factors such as temperature, pressure, and humidity, which can lead to interference with the sensing mechanism.
3. Processing challenges: The processing of CBFM can be challenging due to their tendency to agglomerate or form random structures, which can affect their optical properties and sensing performance.

4. Fabrication complexity: The fabrication of CBFM for optical sensing applications can be complex and require specialized equipment and expertise.
5. Safety concerns: Some CBFM, such as CNTs, have shown potential health risks due to their nanoscale size and biopersistence, which can limit their use in certain applications.

5.2 Future Directions

The CBFM for optical sensors is a rapidly growing area of research, and there are many exciting future directions for this field.

Here are some potential areas of future development;

1. Improved sensitivity and selectivity: One major area of focus is improving the sensitivity and selectivity of CBFM for optical sensors. This can be achieved through the development of new materials, functionalization strategies, and sensing mechanisms.
2. Integration with advanced technologies: Another area of development is the integration of carbon-based optical sensors with other advanced technologies, such as microfluidics, nanotechnology, and artificial intelligence. This could enable the development of highly sensitive, selective, and automated sensing systems for various applications.
3. Multi-modal sensing: CBFM for optical sensors can be designed to sense multiple analytes using different sensing mechanisms, such as fluorescence, absorption, and scattering. Future directions could involve the development of multi-modal sensing platforms that can detect multiple analytes simultaneously.
4. Biocompatibility: CBFM for optical sensors have potential applications in biomedicine, but their biocompatibility needs to be improved to avoid toxicity concerns. Future development could focus on the development of biocompatible carbon-based sensors for biomedical applications.
5. Scalability and commercialization: As CBFM for optical sensors moves from the research laboratory to practical applications, scalability, and commercialization become increasingly important. Future development could focus on developing cost-effective and scalable fabrication methods for CBFM for optical sensors, enabling their widespread use in various applications.

Overall, ongoing research and development in CBFM are expected to lead to the development of novel optical sensing platforms with enhanced sensitivity, selectivity, and portability. The future development of these materials will have significant implications for a wide range of applications, including environmental monitoring, biomedical sensing, food safety monitoring, and structural health monitoring.

6 Conclusion

CBFM have emerged as a promising platform for optical sensing applications due to their unique optical and surface properties. CNTs, graphene, C-dots, and fullerenes are some of the commonly used CBFM for optical sensing applications. These materials can be engineered to exhibit enhanced sensitivity, selectivity, and portability for various sensing applications, including environmental monitoring, biomedical sensing, food safety monitoring, chemical sensing, and structural health monitoring, gas sensing, biosensing, and fluorescence-based sensing. Graphene, CNTs, and C-dots have been extensively studied for their potential use in optical sensing applications. GBOS has been developed for the detection of various gases including nitrogen dioxide, ammonia, and carbon monoxide. CNT-BOS has been developed for the detection of biological molecules such as proteins, DNA, and viruses. C-dots have been used for the detection of analytes such as metal ions, organic molecules, and biological molecules. The unique optical and electronic properties of these CBFMs make them ideal for optical sensing applications. Graphene has a high surface area and excellent electrical conductivity, making it an excellent material for gas sensing. CNTs possess unique electrical and mechanical properties that make them ideal for biosensing applications. C-dots have high photoluminescence quantum yield and tunable optical properties, making them ideal for fluorescence-based sensing applications. One of the key advantages of carbon-based sensors is their high sensitivity. Due to their unique properties, these sensors can detect low concentrations of analytes with high accuracy. Carbon-based sensors are shown to exhibit excellent selectivity, meaning that they can distinguish between different analytes, making them ideal for use in a wide range of sensing applications. The potential applications of CBFM for optical sensing are immense. Carbon-based sensors have potential applications in environmental monitoring, medical diagnostics, and industrial process control. Carbon-based sensors are also relatively inexpensive and can be easily produced in large quantities, making them attractive for commercial applications. Further research is needed to optimize the fabrication processes and enhance the sensitivity and selectivity of carbon-based sensors. The potential for CBFM in optical sensing is vast, and continued research and development are expected to play a critical role in the development of new sensing technologies.

In conclusion, CBFM has emerged as highly attractive candidate for optical sensing applications. The use of these materials has opened new possibilities for the development of highly sensitive and selective sensors. Continued research in this field will undoubtedly lead to the development of new and improved CBFM, expanding the range of applications for optical sensing and leading to exciting new developments in the field.

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Metallopolymer-Based Sensor for Hazardous Gases

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Abstract The hybrid structure of metallopolymers has garnered significant attention from researchers and the scientific community worldwide due to its multifunctional, biodegradable, and highly proficient elastic-tensile properties. Their periodic structure and innovative architecture make them potentially suitable for the synthesis of low-cost energy harvesting, sensing, and optoelectronics devices. Furthermore, their larger surface area and homogeneity enhance their physicochemical properties, making them ideal candidates for rapid response, quick recovery, low power consumption, and, therefore, superior sensing materials compared to other options. Hazardous gases such as nitrogen oxides (NO_x), sulfur oxides (SO_x), methane (CH_4), and carbon monoxide (CO) pose life-threatening risks and must be detected at an early stage of leakage. Metallopolymer-based gas sensors play a vital role in effectively detecting these gases. In this chapter, we will discuss the current achievements and upcoming challenges related to metallopolymers as functional materials for advanced gas sensing applications in environmental monitoring.

Keywords Energy harvesting · Sensing · Response · Metallopolymer

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1 Introduction

Globally, one of the foremost challenges confronting the scientific community is the significant increase in the emission of hazardous gases. With the growth of civilization, industrialization, and the widespread adoption of fuel-based transportation, there has been a substantial rise in the release of harmful gases, including carbon dioxide, carbon monoxide, sulfate-based gases, and other volatile organic compounds. These emissions have deleterious effects on the global environment and pose a significant threat to living organisms. Consequently, this issue has garnered the attention of scholars worldwide and has spurred them to search for suitable sensor materials for the early-stage detection of hazardous gases. Real-time monitoring of hazardous gases is imperative, and this can only be achieved using reliable gas sensor devices. These sensors should be strategically deployed in industries, refineries, medical diagnostic facilities, and sectors related to space and defense. The primary objective is to ensure the precise and accurate detection of harmful gases, enabling timely interventions to prevent any potential tragedies resulting from gas leaks.

Various conventional gas sensors based on metals, metal oxides, and ceramics have been used for several decades for this purpose [1]. Recently, metallopolymers have emerged as potential candidates for sensing devices. These remarkable metallopolymers find applications in various important fields such as solar cells, sensors, polymer-based LEDs, memory devices, biomedical applications, catalysis, and more [2], as listed in Fig. 1. Metallopolymers are innovative hybrid materials in which metals are incorporated into an organic polymer matrix. This incorporation of inorganic elements into an organic matrix imparts significant advantages, making them superior to conventional gas sensors based on other materials [3, 4]. Historically, the first synthesized metallopolymer, Poly(vinyl ferrocene), was discovered by Arimoto et al. in 1955 [5]. Despite their fascinating and novel properties, limited research has been conducted on these hybrid structures due to a lack of suitable characterization methods. This factor led to their relative obscurity until the late 1990s. With advancements in synthesis methods, control techniques, and the development of sophisticated analytical instrumentation facilities, the study and fabrication of polymer-based materials have become increasingly smooth [3, 6–8]. For example, in 1990, Forster et al. employed a stepwise polymerization route for the synthesis of metallopolymers consisting of osmium and ruthenium, which were characterized using UV–Vis spectroscopy [9]. Subsequently, the incorporation of metals into polymer hybrid structures emerged as a significant branch of polymer science in the twentieth century. In 2005, Athawale et al. published a study on PANI/Pd nanocomposites formed through the reflux process [10]. They exposed these nanocomposites to various aliphatic alcohol vapours, including isopropanol, and observed that PANI/Pd nanocomposite-based sensors exhibited high sensitivity, exceptional selectivity, and rapid response to methanol vapour. Metallopolymer-based gas sensors, owing to their enhanced optoelectronic properties, appear to outperform conventional gas sensors. Furthermore, doping metal nanoparticles into the polymer matrix enables room-temperature adsorption and desorption of reducing gases such as H_2, CO, and NH_3 [11–15]. Compared to other types of gas sensing devices, metallopolymer-based gas sensors offer the versatility of multiplex detection for various hazardous gases [8]. It has been demonstrated that the composition, size, and shape of the metal nanophase significantly influence the electrical conductivity and other properties of the composites used in gas sensor devices [16]. Hong et al. [17] created nanocomposites of PPy/Pd in 2009 by initially gas-phase polymerizing pyrrole and subsequently reducing Pd ions in a solution. They discovered that the structure of the composite membrane is significantly influenced by factors such as the concentration, absorption, and proportion of reactants, the polymerization reaction time, and the quantity of polymer additives. Subsequently, they calculated the nanocomposite's sensitivity to NH_3 detection. In 2013, Zhang et al. [18] implemented a one-pot method to produce PPy/Gold nanocomposites with uniformly distributed gold NPs on PPy. The size of the gold NPs was significantly reduced by the addition of lysine. Another crucial point to consider, aside from NP size, is NP concentration. Choudhury [19] synthesized PANI/Ag nanocomposites in 2009 using an in-situ chemical polymerization method at concentrations ranging from 0.5 to 2.5 mol% Ag. Their research revealed that the concentration of silver NPs had a substantial impact on the sensitivity and response/recovery time of the PANI/Ag nanocomposite-based sensor. Furthermore, the dielectric and conductivity properties of PANI/Ag nanocomposites were greatly superior to those of pure PANI, with AC conductivity being approximately 100 times higher. The PANI/Ag nanocomposites-based sensors also exhibited faster and more reversible ethanol detection capabilities. In general, metals often exist in the form of NPs in metal-conducting polymer nanocomposite systems, whereas conductive polymers are typically in the form of thin films. However, quantum-confined metal-incorporated polymer structures in one or two dimensions can also benefit from their high surface-to-volume ratio to enhance the performance of gas sensors [20–22].

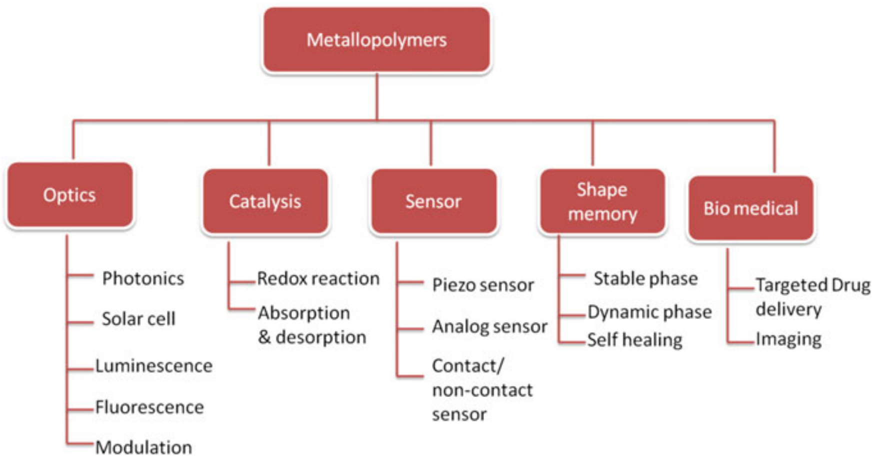

Fig. 1 Illustration of various applications of metallopolymers and their respective field

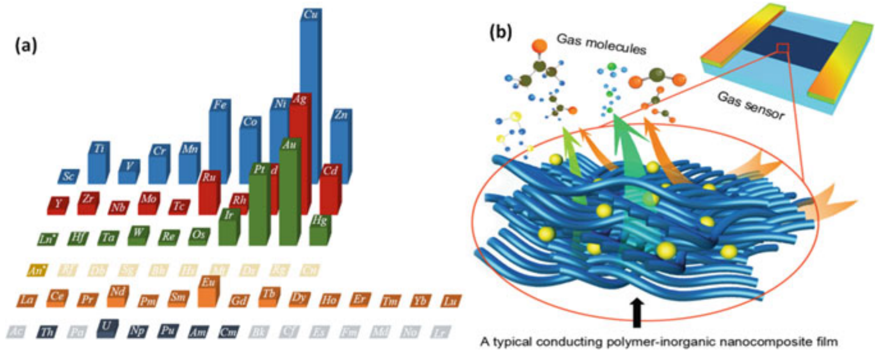

Fig. 2 **a** Schematic representation of d-and f-group metal utilized with polymers and their rate of publication. Reprint with permission from [2]. Copyright (2021) Elsevier. **b** Representation of polymer-inorganic nanocomposite film for gas sensing, reproduced from [16]. Copyright (2020) Taylor & Francis

The market for gas sensors is currently estimated to be worth $500 million annually and is expanding at a 10% annual rate [23]. Furthermore, in Fig. 2a, various d and f-block metals incorporated into a polymer matrix are revealed, along with their publication rates. Additionally, in Fig. 2b, there is a schematic representation of a typical inorganic-polymer nanocomposite film for gas sensing purposes.

Furthermore, the market's recent expansion has been facilitated by smaller gas sensors based on metallopolymers. These sensors have contributed to reducing the cost per unit of sensors.

2 Classification of Hazardous Gases

Hazardous gases can pose significant risks to human health and the environment due to their toxicity, flammability, noxious properties, or corrosive nature, which depend on their specific characteristics and concentration levels. These gases can have detrimental effects, directly impacting the neurological and cardiovascular systems of living organisms [24]. Hazardous gases and vapors, including but not limited to toxic industrial gases (such as NH_3, H_2S, CO_x, NO_x), organic volatile compounds, and radioactive species, pose serious threats to both the environment and human health. The primary sources of these dangerous emissions into the environment are anthropogenic and encompass industrial facilities, power plants, domestic sources, and the burning of fossil fuels. In Fig. 3, a classification of hazardous gases is presented, emphasizing the importance of early detection to prevent accidents. This chapter will delve into various categories of hazardous gases for a comprehensive understanding of their risks and implications.

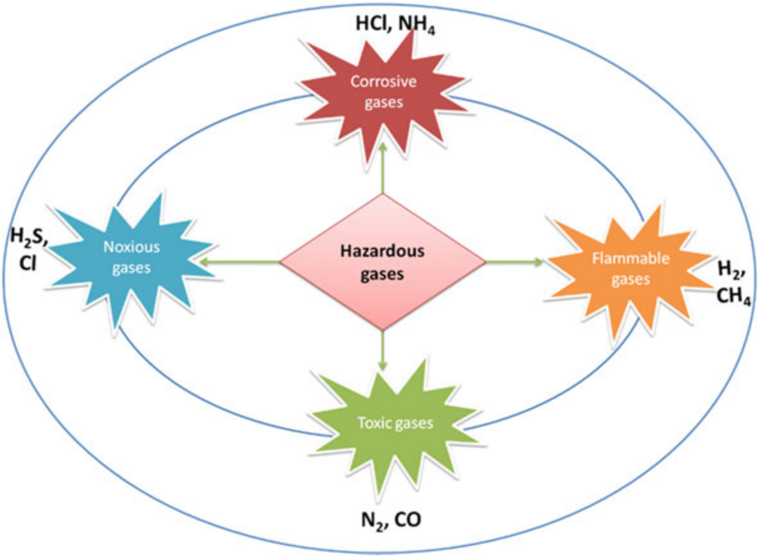

Fig. 3 Schematic representation of types of various hazardous gases

2.1 Toxic Gases

Asphyxiants or toxic gases for example carbon monoxide are dangerous and can lead to death by various mechanisms, including the depletion of oxygen in the environment. These gases interfere with the body's ability to access oxygen, ultimately resulting in fatalities.

2.2 Corrosive Gases

Corrosive gases are harmful as they can directly impact human tissues. Additionally, these gases can damage metals and other construction materials. Examples include hydrochloric acid, ammonia, and sulfur dioxide, among others.

2.3 Flammable Gases

When flammable gases are combined in the proper ratios with air or oxygen, they can become explosive. Consequently, gas mixture explosions can occur, posing a significant threat to the safety of public property and individuals working in the chemical industrial sector. Hydrogen, methane, propane, ethylene, acetylene, and ethane are a few examples of flammable gases.

2.4 Noxious Gases

Noxious gases, such as hydrogen sulfide, sometimes referred to as sewage gas, comprise a group of hazardous substances. Hydrogen sulfide is a colorless, highly flammable gas that poses significant dangers. Even in small quantities, it emits a strong odor resembling "rotten eggs." These gases find prominent usage in various industrial processes, including mining, pulp and paper manufacturing, oil and gas refining, and other industrial operations. In contrast, they can also occur naturally in environments like sewers, volcanoes, and pits. The primary sources of these types of gases, as indicated by [25], are refineries, power plants, petrochemical processes, and effluent treatment facilities.

3 Categories of Metallopolymer

Wolf proposed a classification system for metallopolymers based on the positioning of metal complexes within the polymer matrix. This classification includes three categories: Type I, Type II, and Type III, which are determined by the method of incorporating metals into the hybrid structure [26].

In the classification of Type-I metallopolymer, a metal complex is attached to the polymer backbone through the association of an alkyl group. This attachment is made under the condition that the physiochemical properties of the metal group must be identical to those of the polymer matrix. Figure 4a represents a Type-I metallopolymer, which consists of an inorganic metal compound linked to the backbone of a polymer block.

In the Type-II metallopolymer classification, the metal complex and the polymer backbone are electronically coupled to each other, as depicted in Fig. 4b. These hybrid structures exhibit both feasible and tunable properties due to the presence of a redox-active system within the organic–inorganic framework. Bipyridyl ligands are particularly well-suited for attaching metal ions to the hybrid polymer backbone and play a crucial role in facilitating strong electronic interactions between the metal center and the bipyridyl groups within the hybrid polymer backbone.

For the Type-III metallopolymer category (Fig. 4c), the metal center is directly bonded to the hybrid polymer backbone. In this arrangement, dominant electronic interactions occur between the metal group and the polymer backbone. Moreover, the metal center can facilitate intramolecular charge movement. These metallopolymers are attractive materials for energy harvesting devices, where high charge carrier mobilities are one of the fundamental requirements.

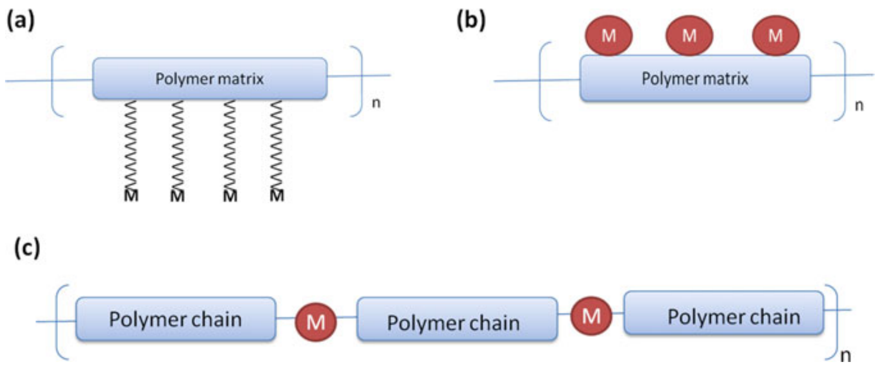

Fig. 4 **a**–**c** Schematic diagram of Type I, II, and III metallopolymer

4 Characteristics of Metallopolymer-Based Gas Sensors

4.1 Degree of Dispersion

The majority of the currently used methods for creating metallopolymers are based on condensation and dispersion techniques [27]. In the primary instance, phase change results in the spontaneous assembly of a polymer matrix from individual molecules. The second approach posits that metallopolymers are formed during the dispersion (or breakdown) of a macroscopic phase. These methods enable the production of metal-incorporated polymers with varying degrees of dispersion for gas sensing. Furthermore, the cost of any material, from its raw materials to its final hybrid structure, is influenced by its processability. The processability of metallopolymer-based gas sensors may be affected by the cost of producing nanocarriers and the availability of raw materials for enzyme carriers.

4.2 High Mobility and Larger Surface Area

The mobility of metallopolymers is exceptionally high, which results in a significant number of charge carriers available for interaction when exposed to target gases. Furthermore, metallopolymers offer a substantial advantage over conventional materials due to their larger surface-to-volume ratio [2]. These characteristics render them highly suitable candidates for gas-sensing devices.

4.3 Porosity

Depending on the available coordination sites on the metal and their position within the organic matrix, high porosity can be achieved in these hybrid structures. Pores play a crucial role in defining the matrix's capacity for stabilization. These pores serve as conduits, allowing nanoparticles or their precursors to infiltrate the polymer bulk. Additionally, the presence of nanoparticles may induce structural distortions in the polymer. Several parameters can influence porosity, specific surface area, and pore radius [28].

4.4 Nucleation

The ratio between nucleation and crystallization rates plays a critical role in determining the ultimate hybrid morphology during the synthesis of metallopolymer, which is a thermodynamically driven process. The high energy of the particles produced can be attributed to the presence of uncompensated linkages on many surface atoms. By calculating their critical size and identifying controllable variables, the thermodynamic method facilitates the analysis of the conditions leading to the formation of nuclei in the new phase. The distribution function of metal-incorporated polymer structure sizes is often defined using kinetic equations, which are frequently employed to elucidate experimental data [29].

4.5 Basic Aspect of Gas Sensor

The presence of a particular gas in the atmosphere is detected by a device known as a gas sensor. Such devices consist of a sensing layer made from a prepared material in the form of a thin film and can detect alterations in resistance when exposed to hazardous gases. This type of sensor is primarily referred to as a chemoresistive gas sensor [30]. The change in resistance results in electronic variations, which occur during the interaction between the sensing layer and the hazardous gas. Figure 5 depicts a schematic of an Interdigital Microelectrode (IDE) comprising a polymer matrix with incorporated Co metal for NO gas detection.

In Fig. 6, a general assembly of a gas sensor is shown, consisting of a transducer, a receptor, and a responsive circuit. Broadly, gas sensors are categorized based on the transducer used and subcategorized by the type of thin sensing materials [31].

$$\text{Gas Response (S)} = \frac{R_a}{R_g} \text{ (for reducing gases)}$$

Or

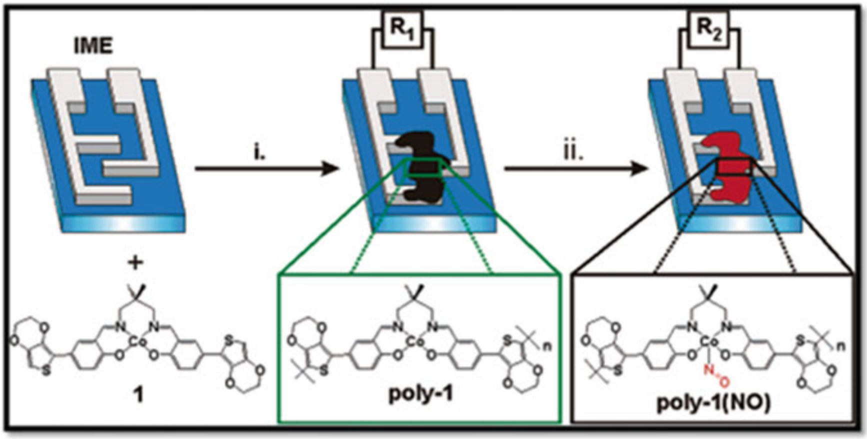

Fig. 5 Schematic illustration of the fabrication of conducting metallopolymer/electrode devices: (i) electropolymerization of Co containing monomer (1) across interdigitated microelectrodes (IME), (ii) chemoresistive response to NO gas exposure, reproduced from [31]. Copyright (2006) American Chemical Society

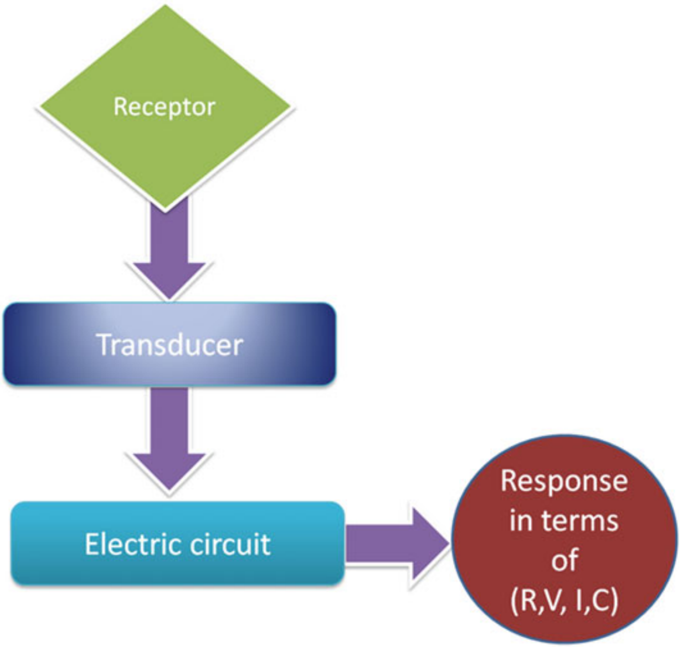

Fig. 6 Schematic setup of transducer and sensing material with electric components

$$(S) = \frac{R_g}{R_a} \text{ (for oxidizing gases)}$$

Furthermore, on a logarithmic scale, there exists a linear relationship between Rg and the pressure of hazardous gases, a phenomenon known as the power law [32]. A distinct adsorption equilibrium forms when thin metallopolymer films are exposed to gases other than environmental reference air. In this equilibrium, some of the new gas components (analytes) in the carrier gas diffuse into the film. When the analyte exits the gas phase, this process can be reversed, as illustrated in Fig. 7. The addition of analyte gas during its presence can significantly alter the physical, electrical, optical, and color properties of the film. This includes changes in dielectric constants and colors. Besides, the operating temperature plays a crucial role in the reliability of response and recovery times. With increasing temperature, the response and recovery times are extended when exposed to reducing gases. Conversely, when interacting with oxidizing gases, the gas response decreases with increasing temperature. This reverse behavior occurs in oxidizing gases due to variations in the energy band resulting from gas molecule adsorption on the surface [33]. There is another important classification of gas sensors where capacitance and applied voltage are the main factors influencing gas sensing behavior. Typically, solid dielectric materials and electrolytes are used in this context [24]. For gas-phase testing, metallopolymer films are deposited over interdigital Pt or Sn electrodes using methods such as sputtering, sol–gel, or chemical vapor deposition (CVD) [31]. Figure 8 illustrates schematic methods for the formation of metallopolymer films through chemical processes.

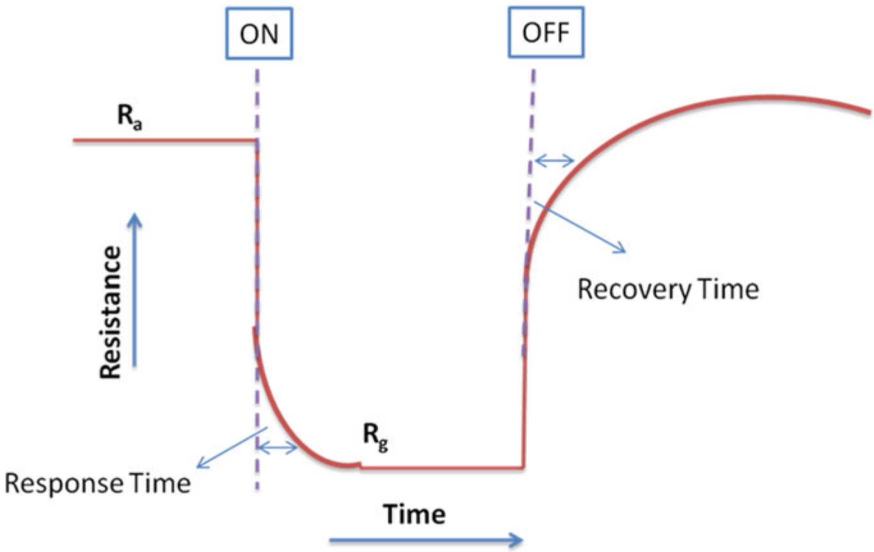

Fig. 7 Schematic illustration of recovery and response signal on exposure to gas

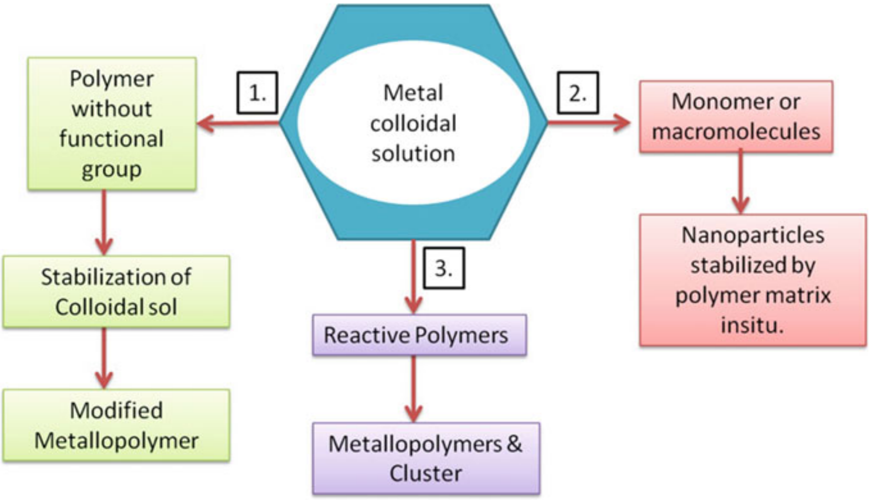

Fig. 8 Illustration of chemical routes for the synthesis of metallopolymers

The synthesis routes described above represent facile approaches for fabricating metallopolymers intended for gas-sensing purposes. The final hybrid structure's grain size depends on several factors, including the choice of the host polymer matrix, the selection of linkers, and the specific metal ion chosen for incorporation. Furthermore, it is possible to easily adjust the cluster particle size of the metallopolymers and enhance their recovery and response characteristics by modifying the reaction conditions and altering the associated ligands.

5 Concept of Stabilization

The stabilization of metals using hybrid polymers involves consideration of several key factors, including the dependence of metal nanoparticles in a liquid medium, the settling capability of the polymer network, and the adsorption of polymers onto metal complexes. The high chemical activity at metal–polymer interfaces can lead to numerous spontaneous reactions [34]. Polymer colloidal science, in its current state, encompasses the stabilization of metal nanoparticles by high-molecular-weight compounds, representing a significant subfield. This area of study delves into the development of highly sophisticated interfaces within dispersed systems, examining their kinetic and aggregation stability, surface topographical phenomena arising from interactions, and the adsorption of polymers from liquids onto solid surfaces. Colloidal solutions containing both metal and polymer are characterized by relatively low stability, primarily due to their larger particle sizes and considerable free surface energy [35]. Solutions with metal-incorporated polymers achieve stability through one of two mechanisms. Kinetic stability pertains to the ability of the system to resist gravitational forces. As particle size increases, the sustainability of such structures significantly decreases. When the rate of particle settling under the influence of gravity is so slow that it can be ignored, the system is considered kinematically stable. Another form of stabilization is referred to as aggregate stability, which concerns the system's capacity to maintain a diverse range of particle sizes [36]. This type of stability is associated with the capacity of nanoparticles to form large aggregates and adsorb low-molecular-weight ions from solutions onto their surfaces, leading to the formation of an adsorption layer. Metal-incorporated polymer colloidal solutions are broadly categorized into lyophobic and lyophilic types. Lyophilic systems are thermodynamically stable, characterized by negative Gibbs free energy changes. Electrostatic (charged) stabilization is a conventional method for achieving kinetic stability in lyophobic particles. These processes provide stability by creating a repulsion potential that exceeds the energy of colloidal particle aggregation [37]. The stabilization process of metal complexes by polymers can be elucidated by the "molecular solder" hypothesis, also known as adhesive interactions between constituent components. The structural and mechanical aspects of the sustainability of dispersed coagulation structures are fundamental to this theory. The degree of steric stabilization varies as structures are formed, ranging from those with only adsorption layers to those covering the entire volume of the microemulsion. Polymer layers begin to interact when two metal nanoparticles surrounded by adsorbed soluble polymer chains approach each other at a distance smaller than the average thickness of the adsorption layers. In most cases, this interaction results in repulsion and steric stabilization. Efforts have been made to consistently define the nature and quantify the magnitude of this steric stabilization. Typically, this issue is examined in terms of how the Gibbs free energy changes when two molecules, initially at infinite distances from each other, approach each other closely while being coated by an adsorbed polymer layer. Adsorption of polyelectrolytes is a more intricate process compared to that of nonpolar polymers. Two crucial factors in determining the extent of polyelectrolyte adsorption on the charged surface of a nanoparticle are the degree of polyelectrolyte screening and the charge density on the hybrid matrix's surface. The intrinsic characteristics of colloidal particles in a solution play a significant role in reducing specific electrolyte adsorption. Polyelectrolytes can achieve both charge and steric stabilization, adding complexity to the process. Several theoretical frameworks have been proposed to elucidate the mechanism of metallopolymers' stabilization by polyelectrolytes. For example, researchers have examined the influence of homopolymer-based polyelectrolytes at various low-molecular-electrolyte concentrations in liquid [38]. Numerous models have explored the stabilization of metal surfaces by charged monomer units and uncharged block copolymers in the presence of a preferential fluid. These investigations have considered the nature of the liquid and the extent of low-molecular substance adsorption on the metal surface [39]. Silbert et al. [40] have researched polyelectrolyte and uncharged block-copolymer adsorption, focusing particularly on non-selective solvents [41].

5.1 Growth of Metal Incorporated Polymers

Inhomogeneities and different phases are generated at the micro level during the manufacturing of metal-polymer composites through a series of intricate physicochemical reactions. These processes have been extensively studied using various metal-polymer systems, including triplet systems and those containing bimetallic elements [27]. Preliminary polymer formulation plays a pivotal role in the preparation of structurally advanced materials. It involves the utilization of a polymer hybrid matrix with molecularly distributed metal salts. Nevertheless, the formation of complex structures, chemical metal compounds, and other metal complexes, along with chelate cycles of varying compositions involving polymer functional groups, is a critical factor that influences the degree of interaction between the polymer and the metal.

5.2 Self-assembly of Metallopolymers

Over the past few years, there has been significant research focused on the self-assembly of polymers. Consequently, researchers have designed and synthesized several diblock and triblock copolymers, closely examining their hybrid structures [42]. The fact that most metal complexes carry a charge can facilitate the self-assembly mechanism [43]. Moreover, the introduction of heavy metal ions can enhance their contrast properties. Table 1 presents various self-assembled metallopolymers investigated by researchers. Numerous metals, including Ni, Ru, Pd, and Au, among others, are incorporated into the polymer matrix to develop these self-assembled metallopolymers.

5.3 Ligands

By adjusting the metal ion or pH of the system, metal-ligand (M-L) bonds provide a wide range of adaptability in terms of bond strength and binding kinetics, leading to the development of polymers with controllable mechanical properties. This capability enables the synthesis of metallopolymers using various extensively studied M-L pairs [56]. In recent years, numerous supramolecular metallopolymers have gained widespread use as functional materials with promising features. In Table 2, we present some common ligands and their associated metallopolymers.

Table 1 Development of self-assembled metallopolymers and their investigation by various researchers

Serial number	Research group	Self-assembled metallopolymer	Reference
1	Guillet et al.	Ni@ PEG/PS	[44]
2	Mugemana et al.	Ru@ PEG/PS	[45]
3	Yamada et al.	Pd@MEPI	[46]
4	Mohd Yusoff et al.	Pd@KAPs (Ph-PPh3)	[47]
5	Weck et al.	Pd@PS (polymethacrylamide)	[48]
6	Liu et al.	Pd@OAC	[49]
7	Karimi et al.	Pd@NHC/MCOP	[50]
8	Peris et al.	Au@tris(N-hetrocyclic177carbene)/acetylide	[51]
9	Jiang et al.	Pd@ZIF-8	[52]
10	Kajiwara et al.	Ru@PCP	[53]
11	Xu et al.	Au@UIO-67	[54]
12	Elmas et al.	Pt@PGM	[55]

Table 2 Various Ligands and Associated Metallopolymer Studied

Serial number	Ligand	Metallopolymer	Reference
1	Phenol	V^{3+}, Fe^{3+}, Al^{3+}@3,4-dihydroxyphenylalamine	[57]
2	Carboxylic acid	Zn@polydimethylsiloxane	[58]
3	Carboxylic acid	Al@polysiloxane	[59]
4	Pyridine	Zn(II)@diiminopyridine	[60]
5	Terpyridine	Cd(II)@2,2,6,terpyridine	[61]
6	Pyridine-dicarboxamide	Fe(II)@PDMS/PDCA	[62]
7	Azoles	Co(II)triazole pyridine	[63]
8	Urethane	Cu(II)@dimethylglyoxime	[64]

6 Gas Sensor Based on Metallopolymers

6.1 Metallopolymer for Detection of LPG

In-depth research on the frontal polymerization of low-mass molecules, specifically compounds such as butyl or methyl methacrylate/methacrylic acid in the condensed phase, was conducted by Singh et al. in 2012 [65]. The Screen-Printing method was employed to fabricate thick films of synthesized metallopolymers, which were then examined for their ability to detect LPG gas. It is essential to closely investigate the growth of effective and selective LPG sensors tailored to cobalt complexes, as metals within the cobalt family exhibit a high degree of selectivity for LPG sensing.

Thanks to their unique physicochemical properties, materials featuring nanoscale metal particles supported by a polymer matrix have garnered significant attention in recent years. These systems are particularly intriguing for sensing applications due to their high concentration of surface metal atoms in nanosized particles, offering the ability to modify the sensing properties by adjusting their size and surface morphological structure. The proposed mechanism involves the displacement of adsorbed oxygen ions through the formation of water. When LPG molecules interact with the adsorbed oxygen ions on the surface of the synthesized metallopolymer films, combustion products, such as water, are released, resulting in the development of a potential barrier to charge transport. Initially, the surface lacks water vapors, causing environmental oxygen to rapidly adsorb into the dry pores. As the sensor surface adsorbs environmental oxygen, water vapor condenses inside the pores, facilitating the formation of a Schottky barrier. Due to its rapid reaction and recovery times, high sensitivity, and stability, Co/PAAM appears to be a significant metallopolymer for LPG sensing at ambient temperatures, as reported by Singh et al. and other researchers [66].

6.2 *Metallopolymer for Detection of Ammonia Gas*

A crucial aspect of preserving the environment and human health is the measurement and detection of ammonia in the air. Ammonia is easily detectable by the human nose due to its strong odor. It is estimated that the lower limit at which humans can detect ammonia through smell is approximately 55 parts per million (ppm). However, ammonia can still irritate the skin, eyes, and respiratory system at concentrations below this threshold. Therefore, it is essential to utilize highly sensitive instruments for the identification of such substances [17]. Researchers, led by Naidji et al. [28], have developed a metallopolymer by electropolymerizing a homoleptic Ru(II)-terpyridine complex consisting of pyrrole heterocycles. This process results in the creation of a thin polymer coating on the electrode's surface. Metal-containing polythiophenes, polyselenophenes, or polypyrroles with in-chain terpyridines are excellent choices for manufacturing these types of sensor devices because they are straightforward to produce and can be polymerized onto electrode surfaces. Furthermore, in a study by Lou Lan et al. [67], a metallopolymer based on hydroxyapatite (HA) treated with gold nanoparticles was developed for ammonia gas sensing. This involved creating a tube-like HA structure and incorporating gold nanoparticles through a hydrothermal process. The gas sensor's response remained high, even at smaller concentrations such as 50×10^{-6}, with a sensitivity as high as 70.8%. Additionally, Park et al. [68] conducted research on NH_3 chemical sensors based on composites of Ag metal and PEDOT nanotubes. They varied the concentration of $AgNO_3$ from 5 to 40%, resulting in varying concentrations of silver nanoparticles. The Ag/PEDOT nanotube sample with a 5% concentration exhibited the highest sensitivity and the lowest detection range for NH_3. Furthermore, Ag nanowires were employed as a support structure and combined with one-dimensional-nanostructured PANI to create a complex material with a hierarchical network structure for NH_3 detection [69]. The sensitivity of this material increased linearly with rising NH_3 concentrations, which could be as low as 5 ppm. Hierarchical PANI/Ag nanocomposite-based films demonstrated superior selectivity to NH_3 compared to particle-like PANI films.

6.3 Metallopolymer for Detection of CO, CO_2, and NO Gas

Depending on the electrolytic interaction between the metal centers and the polymer strand and the high affinity of the metal centers for binding target ligands, they are exceptionally well-suited for the detection of small molecules such as NO and CO. In their study, Holliday et al. [31] focused on developing a gas-phase detection system for NO, CO, and CO_2 that offers selectivity at the parts-per-million level. This system relies on chemoresistive changes in a metallopolymer film device containing cobalt. To create these films, metallopolymer was synthesized and deposited onto arrays of commercially available interdigitated microelectrodes for gas-phase analysis. These electrodes consist of 50 pairs of interdigitated electrode lines spaced approximately 15 μm apart. These high-surface-area films were then easily loaded with the prepared metallopolymer through electro-polymerization, allowing for direct gas-phase testing within the electrode gaps.

6.4 Metallopolymer for Detection of HCl Gas

Kaneko et al. [70] propose a color-tunable substance in the form of an insulated metallopolymer that responds to an acidic stimulus, leading to conversion from phosphorescence to fluorescence between complementary colors. The entangled polymeric substrate of a Pt-based fluorescent metallopolymer, protected by cyclodextrin, undergoes depolymerization when exposed to HCl due to the acidic dissociation of Pt-acetylide bonds. This process results in the formation of a fluorescent monomer. The thick film of the as-prepared metallopolymer can undergo a phosphorescence-to-fluorescence transition thanks to π–π* transitions. By enhancing the interaction between the synthesized metallopolymer and hydrochloric acid vapors when exposed to UV irradiation, rapid color changes are achieved. These methods are believed to open up new avenues for the development of molecularly accurate printed sensors and next-generation color tunable materials. Additionally, π–π* transitions lead to significant energy differences and, consequently, a remarkable shift in emission wavelength [71].

Table 3 Metallopolymers and their selective study for particular gas detection

Serial number	Year/Reference	Author	Metallopolymer used	Gas detected
1	2006/[31]	Holliday et al.	Co@Poly-EDOT	CO, CO_2, NO_2
2	2012/[65]	Singh et al.	Co@PAAM	LPG
3	2016/[28]	Naidji et al.	Ru@terpyridine	Ammonia
4	2016/[67]	Luo et al.	Au@hydroxypaptite	Ammonia
5	2018/[72]	Pereira et al.	Co(salen) metallopolymer	Molecular oxygen
6	2019/[70]	Kaneko et al.	Pt@phosphorescent metallopolymer	HCl

6.5 Metallopolymer for Molecular Oxygen

Monitoring the movement within biotechnology firms, laboratories, and industries involved in the cultivation of microorganisms often requires the measurement of molecular oxygen. Pereira et al. [72] have developed a sensor platform using a chemical resistor material to create a resistance-based apparatus for detecting dispersed molecular oxygen in fluids. In their research, they electrodeposited a cobalt-selen metallopolymer thin film onto a platinum electrode to establish the chemiresistive circuit element. The sensor's resistance and capacitance characteristics are dependent on the quantity and presence of dissolved oxygen. Metal(salen) complexes undergo electropolymerization to produce π-conjugated metallopolymers with intriguing morphological properties [73]. These poly@metalsalen materials exhibit high stiffness, thermodynamic stability, and catalytic performance when interacting with various organic and inorganic compounds. Coordinating complexes often assemble into molecular nanocolumns when a metallopolymer thin film is deposited onto the surface of a conductive substrate. The sensor developed in this experiment can serve as an alternative for detecting dissolved oxygen in atmospheric samples. Electrochemical impedance spectroscopy was employed on a platinum electrode to measure the impedance of metallo-polymer films. Notably, the film conductivity of the chemiresistor sensor fluctuates in response to changes in dissolved oxygen levels, attributed to significant redox reactions. Table 3 provides examples of metallopolymers and their selective application in the investigation of specific gases.

7 Conclusion

The primary objective of this chapter is to provide an in-depth study of synthesis routes, properties, and characteristics of metallopolymers-based hazardous gas sensors. The motivation for conducting such an intensive study on metallopolymer-based hybrid matrices stems from the unique architecture and novel physicochemical properties of the material, which result from the composition of organic and inorganic systems. Consequently, significant attention has been dedicated to understanding the characteristics, classification, and stabilization of metal incorporation into the hybrid polymer structure. Furthermore, efforts have been made to describe various types of hazardous gases, their impact on living organisms, and the respective gas sensor configurations. In prospect, these materials will find applications in biomaterials, designated drug delivery systems, quality innovation, electronics, and more. Metallopolymers have extensive applications in various fields, including supercapacitors, LEDs, solar cells, and so on. Additionally, metallopolymers-based sensors are known for their precision and accuracy, making it reasonable to assert that our future will witness significant advancements in technologies based on these materials. We have endeavored to present a comprehensive review of current techniques for hybrid metallopolymers, continuous investigation of their properties, and the broad range of their potential applications in the field of gas sensing. Although this process is still under development, it is relatively straightforward and practical to produce metallopolymers by thermally transforming metal-containing precursors incorporated into a polymer matrix through various methods. Without a doubt, these materials will continue to be used and developed in the future.

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Optical Sensors Based on Metal–Organic Frameworks

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Abstract For applications like surface-enhanced Raman spectroscopy (SERS) and luminescence, metal–organic framework (MOF) optical fiber has received a lot of attention. For the planned logical applications, any part of the MOF assembly, counting the metal hubs, natural linkers, and visitor particles, can be utilized as

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a source to make single- or multi-outflow signals. MOFs have developed into an intriguing category of materials in the field of porous materials. The distinct characteristics of these materials are the result of the combination of the properties of organic struts and metal ions/clusters, which are the building blocks of these fascinating designs. MOFs have demonstrated tremendous potential as a variety of species' sensing materials and for numerous other applications. In response to a particular analyte, the signal transduction-induced process in these minuscule, closed nanogaps generates optical output, which may be monitored in several ways. Optical fiber sensors (OFS) based on MOFs have received a lot of attention over the last three decades due to their vast range of monitoring applications in numerous industries, including aerospace, defense, security, civil engineering, and energy. The OS's primary restrictions are as follows: crass sensitivity, massive volume, and large data generation. These difficulties can be overcome by developing advanced data analytics engines powered by recent advances in machine learning (ML) and artificial intelligence (AI). This chapter provides an overview of the evaluation of recent studies of optical fiber sensors as well as the advancements in MOF-based optical detecting of ML and AI technology.

Keywords MOF · Optical sensor · AI and ML optical fiber sensor

1 Introduction

Metal–organic frameworks (MOFs), a new category of sensing ingredients, have emerged in the regime of porous materials [1]. Because of characteristics like their large surface area, structural tunability of the pore metrics, functional nano-spaces, etc., constructed from a variety of metal ion/clusters and sensitive organic ligands, these materials perform better than contemporary alternatives [2]. These permeable plans' repression impact represents an assortment of host-visitor connections with the approaching analytes and gets proper reactions, this can be accomplished with a variety of methods, including atomic emission spectrometry, electrochemical methods, and others [3]. Due to this, many approaches, such as mass spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), electrochemical methods, nuclear ingestion spectrometry, and nuclear emanation spectrometry, as well as others or methods like their high surface area, can be used to accomplish this [4–6]. As fluorometric probes for identifying environmental-relevant organisms, the scientific community has paid close attention to MOFs over time [7]. Additionally, MOFs have demonstrated remarkable ability to detect substances that are harmful to the environment and toxic, making them an emerging possibility for reducing environmental pollution and associated diseases.

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This is because of a few things that control MOFs' sensing mechanisms. Luminescent MOFs (LMOFs) have attracted interest due to their improved guest identification abilities and resulting analyte-specific optical response. Reports on selective analyte detection and turn-on responsive behavior are extremely rare for MOF-based sensors, which typically rely primarily on luminescence quenching mechanisms [8–11]. Inorganic metal particles or group hubs and linkers that include natural ligands and metal–organic structures are used to create a type of permeable hybrid material known as a metal–organic framework (MOF) [12–14]. The high specific surface area, ultrahigh porosity, tunable internal surface property, extremely diverse structure, and acceptable biocompatibility are just a few of the characteristics that set it apart. MOFs are frequently utilized in purification and storage [15], catalysis [16] medication delivery, biomedicine, and chemical sensors and biosensors [17–19]. Because their emission centers can be constructed using "multiple photonic units" derived from inorganic metal ions or cluster nodes, linkers, etc., MOFs are appealing optical sensing materials or its combination to combine inorganic and organic chemistry to demonstrate structural diversity aspects [19–21]. Due to this unique property and adjustable functional sites, MOFs have highly customizable and diverse luminescence that can be used for tailored applications. With rational design, the "multiple optical units" can be manufactured or modified to provide the various luminescence signals previously described. The recent smart appliances comprised in the form of fiber optical sensor, hardware and artificial intelligence (AI) is the most recent digital revolution. Industrial infrastructure is increasingly relying on smart sensors to support intelligent operations including automated asset monitoring, problem detection, and preventive maintenance. The most popular technique for doing this is the evanescent field approach, in which the optical fiber is altered to permit the contained optical modes' evanescent tails to pass through to the outside world [22]. All of which can be used in applications that require specialized capabilities; however, in addition to connecting identification objects for communication with a specific target, The utilization of the functional sites may also be employed to increase contact with emission centers, which can change luminescence characteristics even further. Furthermore, luminous molecules from guests can be encased within the porous structure thanks to its extremely high porosity and adjustable interior surface characteristics.

To give MOFs radiometric, multiplexing strategy, and multi-methodology estimating capacities, one extra component of iridescence might be presented [23–26]. MOFs can be used as signal amplification surfaces or to construct composite substrates by enclosing metallic nanomaterials, both of which are promising materials for SERS approaches. In addition to luminescence, MOFs can also be a promising material. In addition, the large surface area and controlled pore size provide a high capacity intended for adsorbing and intent substances, resulting in a unique sieve effect and a low limit of detection (LOD), both of which enhance selection [25–28].

In general, limiting non-radiative relaxations in MOFs by including stiff functional groups, producing exciplexes or excimers with guest molecules, and so on can elicit a turn-on response. As a result, the current focus of research is on developing suitable sensors that can use LMOFs to elicit a turn-on response. The purpose of this chapter is to present optical nanosensors based on MOFs, with an emphasis on their application in luminescence detection [29–31]. The final topic of discussion is the development of MOF-based nano-sensors for diagnostic and bioanalytical purposes.

2 Advantages of Optical Fiber Sensors Over Conventional Sensors

The headway of FOS innovation innovative work has extended their pertinence to various areas of innovation, including the clinical, compound, and telecom areas. Temperature, chemical changes, electric and magnetic fields, vibrations, strain, movement (position), flow pressure, rotation, radiation liquid level, light intensity, and color are just a few of the physical characteristics they were designed to work with. For extreme climate perseverance, FOS sensors beat conventional electric and electronic sensors concerning unwavering quality and unbending nature. Fiber optic sensors, otherwise called optical fiber sensors, utilize optical fiber as a detecting component. Temperature, pressure, vibrations, displacements, rotations, and substance concentrations can all be determined using these sensors [32, 33]. Strands have a few applications in remote detection since they require no electrical power in the far area and are small in size. In sensitive conditions like noise, high vibration, excessive heat, dampness, and uncertain surroundings, fiber optic sensors excel. These sensors can be precisely placed wherever flexible fibers are required and are small enough to fit in tight spaces. The wavelength shift can be calculated using optical frequency-domain reflectometry. The time delay of fiber optic sensors can be determined using a device with an optical time-domain reflectometer. Figure 1 demonstrates the block diagram of optical fiber sensing and Table 1 various sensing techniques and characteristics of materials are mentioned.

The measurement of physical characteristics like temperature, velocity, displacement, and strain in structures of any size or shape is just one example of the many applications for fiber optic sensors. Night vision cameras, electronic security systems, partial discharge detection, vehicle wheel loads, heritage structures, and bridges and buildings are all monitored in real time.

3 Fiber Optic Sensor Principle

In the early 1960s, fiber optic systems (FOS) for light transmission were created, which bring revolution in transmission era. Current advancements in FOS technology provide qualitative as well as quantitative benefits for continuous surveillance, vast distance measurements as well as prompt identification of threats related to infrastructure deprivation to avoid any type of losses. For real-time detection, measurement and prolonged evaluation, fiber optic-oriented observing and monitoring systems use smoothly dispersed sensing approaches [55]. This makes them enable for early smash

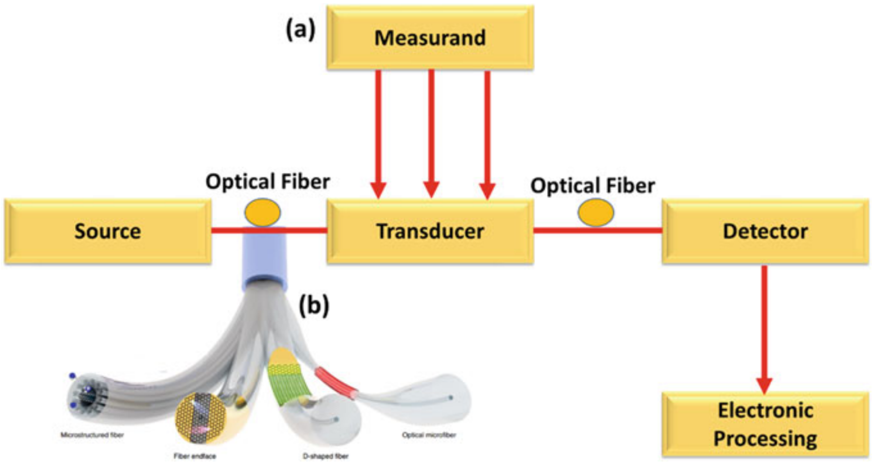

Fig. 1 **a** Block diagram of optical fiber sensing and **b** schematic MOFs of Optical fiber [34]. Open Access (2021) Nature

Table 1 Literature survey of various sensing characteristics

Optical material	Temp. (°C)	Response	Response/recovery time	References
SnO_2-Pt	200	89	20/27 s	[35]
ZnO-PANI	36	13	3.3/9.8 min	[36]
TiO_2/PANI	273	0.63	3.3/3.0 min	[37]
TiO_2/Ni	250	37	–/–	[38]
ZnO/PEDOT: PSS	27	0.58	3.7/3.1 min	[39]
ZnO/MWCNT	30	61	5.8/3 min	[40]
h-BN/-	RT	6.17	55/40 s	[41]
PANI/-	RT	12.10	11/07 s	[42]
ZnO-TiO_2/PANI	30	412	35/54 s	[43]
CdS/-	70	173	5.52/3.46 min	[44]
Ag-$BaTiO_3$/CuO	250	0.28	15/10 min	[45]
CuO-$Cu_xFe_{3-x}O_4$	250	0.50	9.5/– min	[46]
CdO	250	0.01	3.33/5 min	[47]
PEDOT-BPEI	RT	0.03	–/60 min	[48]
$La_{1-x}Sr_xFeO_3$	380	0.25	11/15 min	[49]
ZnO	200	0.03	8/40 s	[50]
ZnO-La (50%)	400	0.65	90/38 s	[51]
SnO_2/PANI/Ag	30	67	1000/900 s	[52]
TiO_2/Zn	RT	2.92	120/– Sec	[53]
Fe_2O_3/ PANI	RT	229	2.35/3.8 min	[54]

up identification, corrective action, and characterization, resulting in rapid remediation. These sensors' morphology and adaptability along with topography enable them to be successfully incorporated into structures for strain monitoring, which might help provide quickly and fast caution signals linked to timely damage detection to avert catastrophic failures. Several methods including Fiber Bragg Gratings (FBG) or scattering relay sensors are developed on the standard of interferometry and reflectometry. These optical standards have been proposed to assess dispersed strains along the intact extent of a fiber [56]. Numerous gratings are placed in discrete places along the fiber as part of the quasi-distributed strain measurement technique known as FBG. It is possible to multiplex several point sensors via a single fiber in order to collect data at a variety of different locations. Additionally, different parameters such as strain and temperature can be measured by different sensors within the same fiber. Three categories of FOS have been established yet: interferometry, reflectometry, and grating-based sensors. FOS technology relay on physical fluctuations of light waves that travel through optical fibers as a result of external inputs or stimuli. These distinctions include those that are responsive to different outside signals, such as the intensity of light, bandwidth/wavelength, phase with one another, and polarization [57].

3.1 Grating-Based Sensor

The impact of grating in mainstay of optical fibers is identified using sensors based on gratings. The grating acts as a slender band filter or transmitor/reflector to modulate assortment of wavelengths also known as Bragg wavelengths, when the light passes through an optical fiber. The warp of FBG sensors by physical factors like strain or temperature affects the fluctuation of grating frequency (υ) and refractive index (μ) especially when FBG is used as a sensing device for strain and temperature monitoring [55]. $\Delta\lambda_B$ is known as shift in Bragg wavelength results from these fluctuations as shown in Fig. 2a.

3.2 Mach–Zehnder and Fabry–Perot-Based Interferometry Sensors

The Mach–Zehnder-based sensors rely on the rule that a solitary light source beam splitter collimates the effectiveness of phase transmit changes illuminated in the midst of two beams. It depends on the length of the routes and how the optical paths alter. To measure a target's changes through phase modulation, a target can be put in the pathways. The Mach–Zehnder-based sensors may be used as a tool for monitoring changes in temperature (ΔT), liquid pressure ($\Delta\rho$), and atmospheric pressure (ΔP) in confined spaces [56, 58, 59]. The Fabry–Perot (FP)-based sensors operate under the

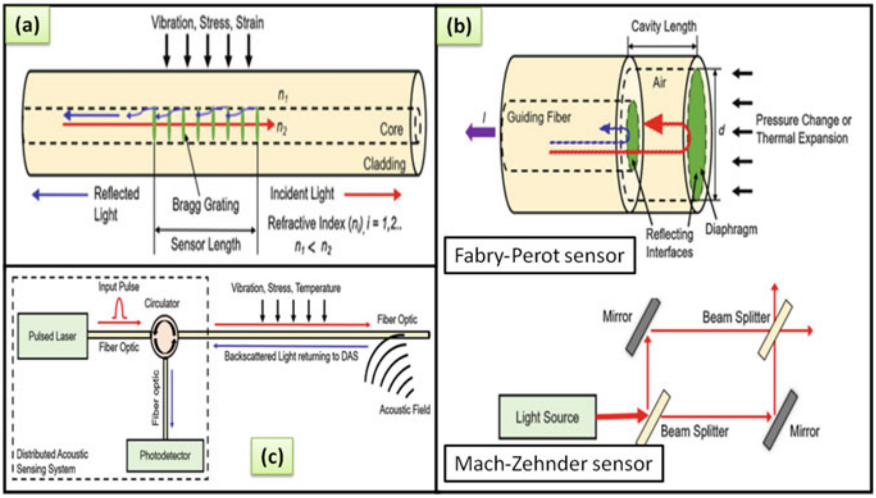

Fig. 2 **a**–**c** Schematic representation of various types of fiber optics sensor including **a** grating-based, **b** interferometry-based, and **c** scattering-based sensor [55]. Copyright (2019) Elsevier

perception, which measures the strength of interference signals that are lit between two analogous reflecting surfaces as represented in Fig. 2b.

3.3 Scattering-Based Sensor

Sensors based on scattering are excellent for long-range and continuous measurements and impart on the optical time zone reflectometry concept. When using a scattering sensing technique, an optical fiber that doubles as a sensor along its length is used to measure the backscattering of optical pulses as shown in Fig. 2c. Here backscattered signal is enhanced, modified, and altered in terms of amplitude, frequency, and phase if physical factors like temperature, strain, or vibration changes at a particular location of the fiber. It is possible to track changes in the environment by keeping an eye on the fluctuations of backscattering signals [60].

4 Detecting Mechanism of MOF-Based Sensors

Metalorganic frameworks (MOFs) are a type of extremely porous materials that are unique and provide wide range in their degree of structural variety, tunable, and broad spectrum of chemiophysical properties [61]. There are practically unlimited combinations conceivable because of the variety of metal ions and topographical structural patterns. The exceptional ease in tuning MOF architecture and physiochemical properties is a significant advantage over other variety of sensing materials. The prospect of consistently predesigning architecture to offer desired qualities is made possible by the ability to quantitatively forecast affinities for host frameworks with superior precision. For a variety of applications such as industrialization, manufacturing operation, toxic and harmful material detection, diagnostics in radioactive sector, for secure work environments and surveillance of the environment there is elementary need of precise and receptive detection of gas and vapor elements which is provided by MOF-based sensors.

MOFs in concurrence with optical sensors provide a potentially identifiable advantage over other types of sensors. There are numerous factors that make MOFs ultra-potential candidates for sensing applications. They are proficient for offering a variety of active sites, such as open metal coordination sites and possess potential interstitial coupling between analytes and host framework either via hydrogen bonds or π–π interactions [62]. In addition to their inherent porosity, there is ease of facilitate transportation, incorporation, as well as encounters with analyte molecules. Therefore, the aforementioned locations may facilitate sensitive and swiftly interaction with the target gas molecules. Several investigations have focused on designing gas sensors using MOFs including chemiresistive sensors, impedance based sensors, luminescent and optical and gravimetric sensors [63, 64]. Optical sensors are distinguished out among these groups for their obvious benefits, including immunity to electromagnetic interferences, distant sensing abilities, user-friendly operations. During the sensing procedure, targeted molecules are frequently preferentially adsorbed. A potential strategy to adapt the pore size and orifice of MOF structure simultaneously and systematically is functionalization of organic ligands. Additionally, it influences the hydrophilic characteristics and hydrophobic nature of MOFs to give rise to the desired adhesion properties of gas molecules. Moreover, MOF defects offer a special way to adjust the adsorption properties.

The two most common lapses include omitted nodes and omitting linkers. These inconsistencies in MOFs can alter the density, as well as the stiffness, mobility, and dimension of the pores in the structure itself. Missing linker flaws in particular result in greater accessibility of metal sites, which might encourage sorption mechanisms. The subsequent sections emphasize on the MOF-oriented optical sensors, which are divided into various categories according to their sensing methods such as: colorimetric, luminescent, and optical index modulation sensing. Optical sensor usually consists of a luminosity source, a sensing element that can interfere with the molecules and detector [62, 65, 66].

MOF colorimetric sensor responses are defined as color changes, whereas fluorescent material sensors are assessed using their intensity counts. Here illumination intensity changes in response to stimulation while in case of MOF optical index-based sensors, the fluctuations in observed indices, such as the peak shift in the reflectance or transmission spectra, determine their sensitivity.

4.1 Mechanism of Chromism-Oriented MOF Sensor

The primary mechanism of MOF-based chromism sensors includes coordination configuration, transition in color, wavelength shift, and receptor-based charge transfer. When guest molecules bind to MOF made of transition metal ions, the color of the material can vary. More specifically, visitor molecule interactions in the midst of unimpregnated metal sites alter the reciprocity structure of the metal ions, influencing their electronic attributes, and ultimately provide for a prominent shift in absorption band of MOF. For instance, H_2O/NH_3 molecules cause the CO_{2+} ion's coordination number to increase from 4 to 6 and as a result, the structure of the ion changes from tetrahedral shape to octahedral shape, changing its color from dark blue to rubby red. VOC sensing may also be done using this kind of approach. Initial stage findings of chromic interactions with a d-block metal-oriented MOF after immersing it in various solvents have been reported by Dzesse et al. [67]. Furthermore, Li et al. investigated a Mn-MOF that exhibited solvatochromic activities towards ketone molecules [68]. Here, ketone molecules caused the original framework to deviate and altered the d-d transition in the visible province. Due to the M-M-to-L charge-transist from the π–π orbital level to π* orbital stage of the organic molecule [69]. For example, a crystal-to-crystal transition of a Cu-based MOF also demonstrated vapochromism shown in Fig. 3a. Given its simple results' visualization and widespread use in modern life, such as pH scales, colorimetry is one of the oldest analytical methods. A responsive core and a prompting molecule combine to produce the chromism phenomenon. The spectrum of intermolecular interactions might encompass the creation of bonds and ligand interaction as well as the weakest interactions caused by Van der Waals forces.

4.2 Mechanism of MOF-Based Magnetic Sensor

Spin crossover MOF and single molecule magnet (SMM)-MOF are the two kinds of magnetic MOFs that are utilized to create magnetic MOF-based sensing switches. These have ability to subsist in both high spin state (HSS) and low spin (LSS) states as transition metal ions have d^4–d^7 electronic configurations, which serve as the metal centroid of MOFs. The geometry, color, impedance, magnetic activity, dielectric factor, loss factor, luminous activity, and other physical properties of spin crossover MOF alter in response to peripheral corporeal and chemical stimuli, switching between two distinctive HSS and LSS zone of metal ions shown in Fig. 3b. There has been an increase in interest in SMMs made of d- and f-block metal complexes due to their potential applications in various sectors. SMM has very sensitive magnetism to external stimuli including pressure, heat, luminescence, and foreign molecules. As they can alter their spin state by changing the surrounding coordination of the core metal so reversible interchange of visiting solvent particles may affect the distances and locations between the ligands and metal ions, as well as the types of interaction

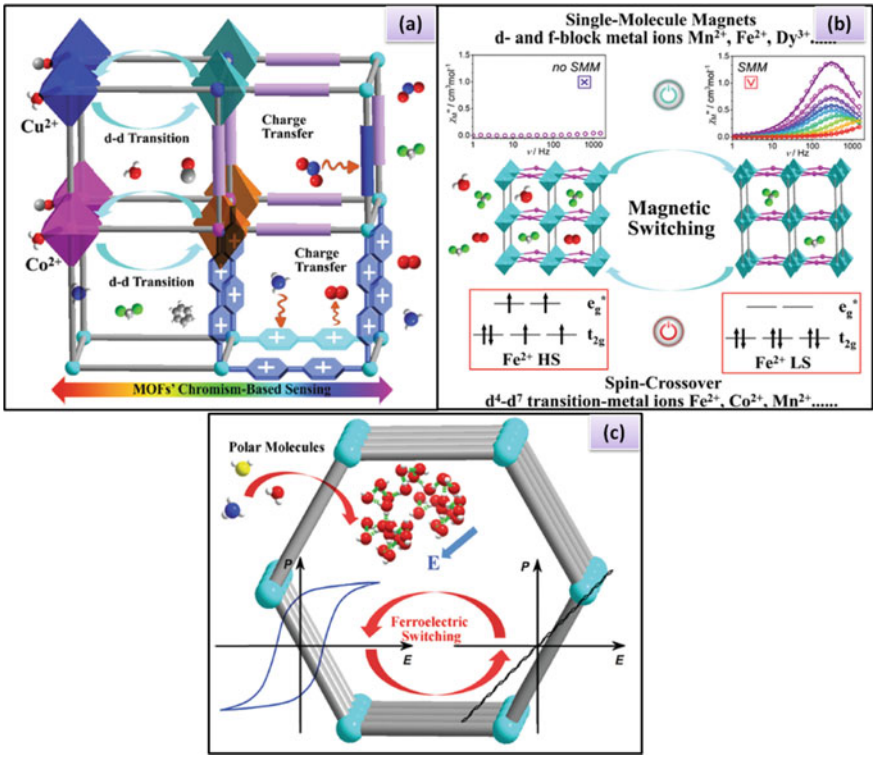

Fig. 3 Various sensing mechanisms of MOF-based gas sensor; **a** chromism **b** magnetic **c** ferroelectric mechanism [67]. Copyright (2020) Royal Society of Chemistry

of the metal center [64]. Additionally, it might result in modifications to the crystal lattice that lead to bond shaping or cleaving, which might affect magnetism.

4.3 Mechanism of Ferroelectric-Oriented MOF Sensor

The interactions between polar analyte molecules and MOFs' hydrogen bonds, which give them ferroelectric nature, are the fundamental principal source of ferroelectric mechanism in MOFs as represented in Fig. 3c. The desorption or adsorption of water molecules, together with ferroelectric toggled characteristics, is the initial stage of the SC-SC transition. The polar point networks must be constituents of the MOF space groups. The MOF should furthermore contain a hydrophilic porosity [65, 66]. The development of MOF ferroelectric switches, thus, constrained by the random nature of MOF-oriented ferroelectric switch synthesis.

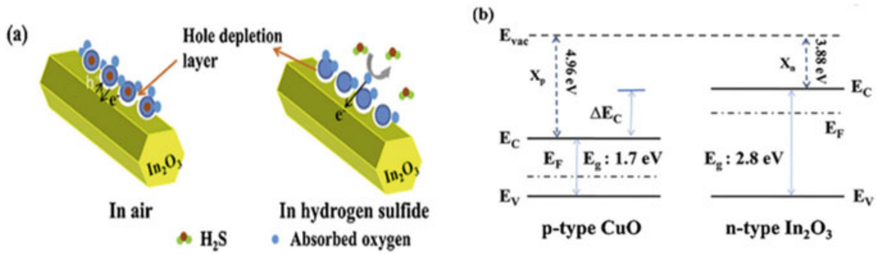

Fig. 4 **a**, **b** Schematic of carrier transportation and gas sensing mechanism for CuO/In_2O_3 sensor @ reused with permission [70]. Copyright (2020) Elsevier

4.4 Mechanism of Chemiresistive-Oriented MOF Sensor

Chemiresistive sensors are based on the elementary operating concept that is a change in the electrical characteristics (resistance, capacitance, or impedance) of the sensing material following by adsorption on contact with the gas molecule under investigation. The resistance of MOF network changes on interaction with gas analyte molecules shown in Fig. 4a, b. These electrical characteristics vary drastically on interaction [70]. The fluctuation in the sensor resistance in the existence of target gas is brought on by the Fermi energy modulation mechanism, which modifies the space charge area at the grain boundaries of thin film and gas molecules.

The electrical properties of MOFs are altered by the redox interaction between gas molecules and host metal sites of tropical organic groups. Moreover, the structural modifications by the chemisorption of gas molecules impact the conductivity of MOFs.

The sensor response [71] can be measured by:

$$S\% = \frac{(R_a - R_g)}{R_a} \times 100 \tag{1}$$

where R_a signifies the resistance in existent of air while R_g refers to resistance in the presence of gas molecule.

4.5 Mechanism of Luminescence-Based MOF Sensor

Significant and one of the most potential subsets of MOFs called luminescent metal–organic frameworks (LMOFs) have a variety of prospective uses in physiochemical monitoring, illumination, electromagnetic optical communications, and biological implant devices. Organic ligands produce luminescence phenomenon in MOF-based sensor. Typically, this class of ligand has sheer π-conjugation network. Organic compounds can glow in one of two main ways: fluorescence or phosphorescence.

The molecular fluorescence has a brief excited state lifetime and belongs to spin permissible transition, which vary from Ist singlet state (S_1) to its ground singlet state (S_0) while the swapping from the spin-forbidden triplet state to the spin-free state, which is the basis for phosphorescence, has excited state durations of 1 μs. There are numerous interactions between gas analytes and the host structure, including Van der Waals interactions and π–π interactions, etc. [61, 69]. Except these fundamental forces, inherent porosity enhances adsorption of analyte. The transition from Q-transit excited domain to ground level, including ligand-to-ligand, metal to ligand, metal to metal and ligand to metal charge impose, provides the basis for charge transfer luminescence. The foundation of these sensors was solid phase impregnation with reagents to accumulate and deliberate the analyte and exhibit color changes in reaction to the analyte for detection.

5 Intensity-Based Fiber Optic Sensor

Intensity-based fiber optic sensors can easily and more affordably replace other fiber optic sensors. Due to its simplicity, possible low cost, low weight, compact dimensions, and electromagnetic invulnerability, these intensity-based fiber optic sensors have significant importance. The theory of total internal reflection serves as the foundation for type of intensity-based fiber-optic sensors [72]. Through the fiber core, light passes before striking the angled end. Nearly all of the light that meets a mirror surface and a medium having a low appropriate index of refraction is reflected and returns through the fiber [73]. An intensity modulation results from some of the light escaping the optical fiber and being lost as the medium's index of refraction approaches that of glass. On striking the core-clad contact at angles greater than its critical angle, incident light totally reflected back and steered in the fiber while the incident light that strikes the interface at miniature angles is contorted into cladding and lost [56, 59]. A light source, an optical interface, a single or more optical fibers, an optical modulator system, detector along with signal processing components are needed as shown in Fig. 5.

However, when a fiber bends there could be losses as a result of the microlending. As a result, the output light amplitude is proportional to the degree of micro-bending. So that the sensor can be used correctly, the micro bending must be identified by detecting variations in emitted light intensity [74, 75].

6 Optical Sensor Types

Optical sensing technology is an interdisciplinary field that combines optical sensors and information science. An optical sensor is a detecting tool that transforms difficult-to-detect information straight into optical information that is simple to spot. It is frequently utilized in both daily living and engineering fields. It has numerous built-in

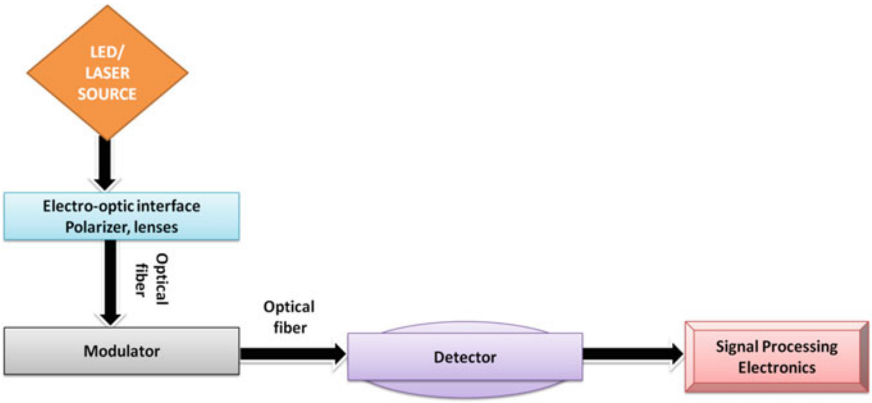

Fig. 5 Schematic block diagram of fiber optical sensor

benefits, including its lightweight, compact size, electromagnetic interference resistance, high sensitivity, reliable operation, chemical inertness, appropriate for remote sensing, protection against electromagnetic interference, and capable to monitor a wide range of chemical and physical parameters with a wide dynamic range.

6.1 Direct Sensors

The medium under vision determines how the illumination is modulated, and the composed light results from direct backscattering from the medium under investigation or medium fluorescence caused by an optical source (e.g., light-based sensors).

6.2 Indirect Sensors

Use an intermediary in response to an interested medium under test property (such as temperature or the presence of an enzyme). Additionally, indirect sensors are frequently grouped into two basic categories based on how the optical fiber is used. If the modulation happens inside the fiber itself, the sensor is said to be intrinsic. Otherwise, it is said to be extrinsic [76, 77].

6.3 Classification of an Optical Sensor

- Distributed sensor
- Extrinsic sensor
- Point sensor
- Intrinsic sensor
- Thru-beam sensor

7 Optical Fiber Sensing Application

Fiber optic sensors (FOS) have attracted much interest for their broad monitoring applications in various manufacturing, consisting of aerospace, defense, security, civil engineering, safety, and energy. Fiber optics sensor (FOS) technology has enormous potential to serve as the foundation of the coming generation of smart sensing systems that provide distributed, long-range, high-accuracy sensing capability for monitoring using several parameters and measurements with resistance to extreme environmental conditions. The primary drawbacks of FOS are (1) cross-sensitivity, (2) massive data creation and volume, (3) slow data processing, (4) the total cost of the sensor and interrogator systems, and (5) a decrease in signal-to-noise ratio across fiber length. These difficulties can be solved by developing robust analytics of data engines made possible by current advancements in machine learning (ML) and artificial intelligence (AI) [78]. Intelligent sensors are everywhere and have many uses, from voice-activated home appliances (such as Alexa, Google Home, etc.)) to the "Industrial Internet of Things (IIoT)." Miniaturization of sensing gear, cheap cloud, high-performance computing access, ample data storage, and analytics technologies. The most current developments in AI and machine learning technologies have all contributed to this revolution. Developing Deep learning research and development (R&D), a branch of machine learning (ML) that uses neural networks with biological inspiration to carry out learning tasks, has been responsible for the advancement of AI since 2012 and its important developments [79]. Machine learning techniques rely on the unique selection and extraction of particular features, while deep neural networks, like CNN, automatically extract the features [80]. DL-based artificial intelligence technologies are gradually showing better performance equivalent to humans in many real-world tasks like image recognition, speech recognition, machine translation, and personalized recommendation [81]. Applications of DL are used in chatbots, healthcare, virtual assistants, and entertainment. Figure 6 displays the possible uses of FOS combined with ML and AI technology.

FOS R&D has advanced significantly over the past two decades and compared to electrical and free space sensors, the technology now offers significant advantages in engineering. Since then, FBG sensors have been widely made after being developed for several real-world applications, including structural health monitoring (SHM, gas, oil, and gas) chemical, biomedical engineering, and ML techniques to

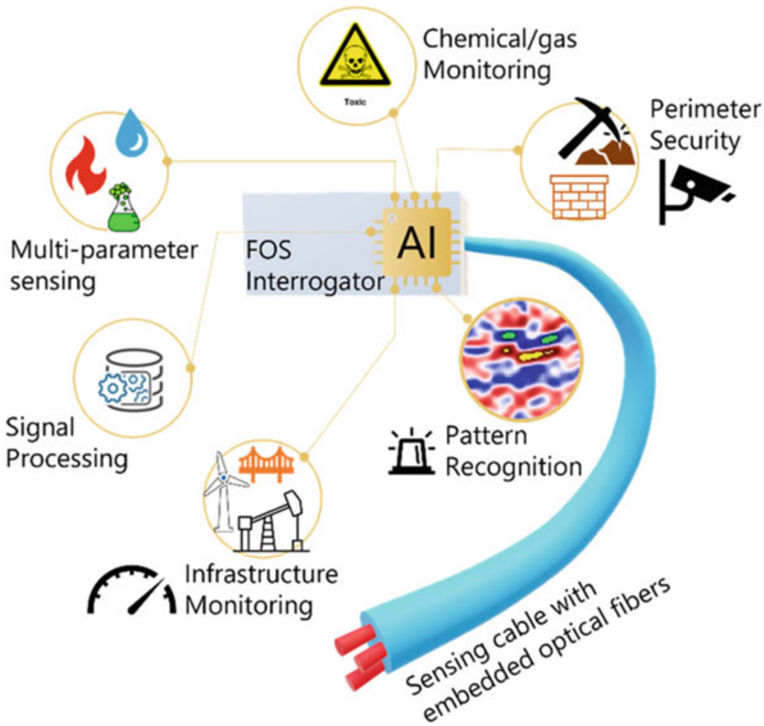

Fig. 6 AI-enhanced FOS and sensing cables with embedded optical fibers and interrogators attached are shown in a schematic for various applications [78]. Open Access (2022) Wiley Online Library

recognize patterns and regularities in data automatically. Additionally, discrete one-mode, multimode single-mode fiber-based sensors provide increased sensitivity and selectivity.

Figure 7 shows the organizational structure and depicts how the tasks involved in developing AI-enabled FOS innovations are interconnected. The several sensors, working theories, and data modalities are described in Sect. 2. In Sect. 3 examines that the difficulties and restrictions of these sensors and the opportunity this creates for the development of ML. Here, emphasize the most current developments in ML and AI that could be helpful to overcome these problems.

Some recent successes in addressing the difficulties associated with analytics of FOS data and event/pattern recognition categorization are highlighted in Sects. 4 and 5. The recent developments in Machine Learning and AI for applications in Fiber Optic Sensors.

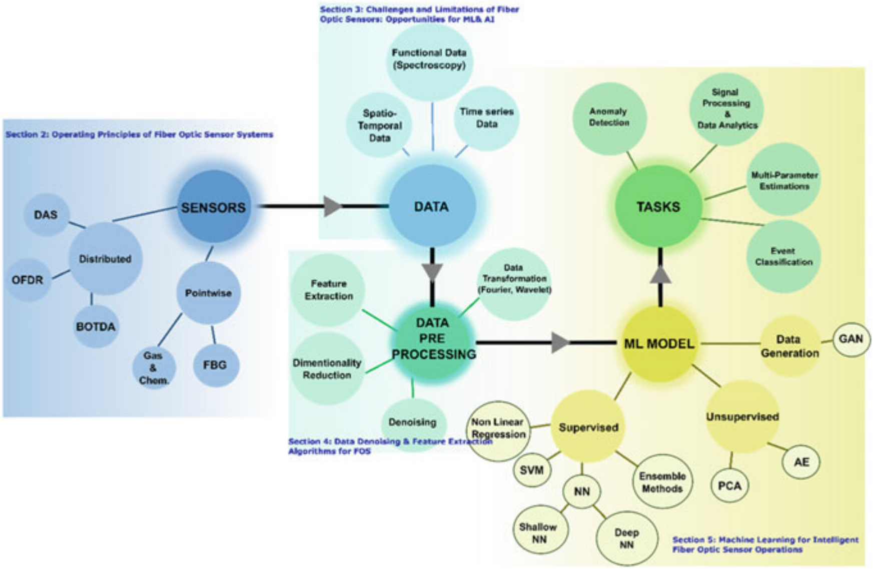

Fig. 7 Shows a hierarchy of the tasks involved in creating intelligent FOS operations [78]. Open Access (2022) Wiley Online Library

7.1 Medical Field

Numerous studies are being conducted worldwide on optical-chemical and biochemical sensing, and these sensors are being used increasingly in industry, biomedicine, environmental monitoring, medicine, and chemical analysis [82]. Because of several factors, optical biosensors are being used more frequently in various areas of medicine. Optical fiber sensors can be inserted into or inside the human body to assess biomedical parameters. Also, many fast-emerging applications utilize FOS for biomedical purposes [83]. For example,

- Oximetry and blood pressure checking
- Monitoring of gastric CO_2
- Monitoring temperature and strain using fiber Bragg gratings
- Monitoring of pressure

Modern medicine has significant problems with effective disease diagnosis and treatment, both depending on the ability and timeliness of detection. Ineffective, unreliable, and expensive detection and real-time monitoring make rapid diagnosis and treatment more expensive. Figure 8 shows the most recent developments in intelligent materials for creating versatile wearable sensors that provide information on their properties, uses, and applications in healthcare. The most recent generation of wearables with AI capabilities for accurate diagnosis, early detection, and making complete and customized clinical decisions [84].

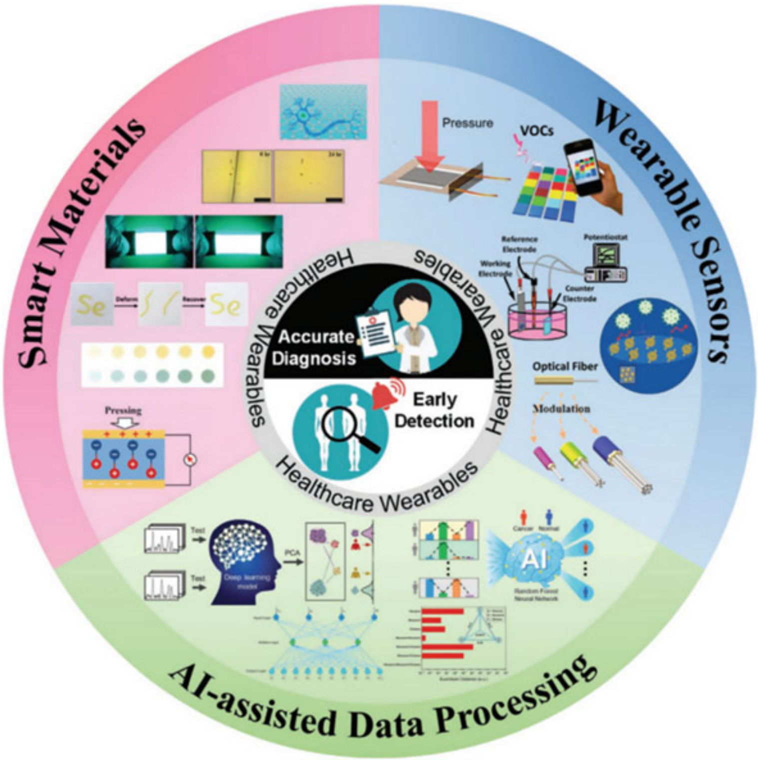

Fig. 8 An overview of the medical wearables for accurate diagnosis and early detection [84]. Copyright (2021) Wiley

7.2 Energy Field

In many different application sectors, there is an increasing need for systems with several sensor nodes. It is becoming increasingly crucial in support of extensive sensor networks and systems to function wirelessly, sustainably, and autonomously. For these reasons, a sensory system with its self-power source that uses its energy to operate the senses and its ability to detect environmental stimuli directly draws much interest [85]. For example, pyroelectric sensors monitor average and repeated pulse energies, Photodiode energy sensors measure low-energy pulse, and a Fast photodetector model, FPS-1, is used to see and measure the temporal properties of laser beams. The PENGs are widely used in biomedical applications, environmental monitoring, artificial intelligence, and biomedical applications as self-powered sensors (Fig. 9).

Energy source monitoring power plants and other structures engaged in producing, transmitting, and converting electricity present several issues that optical sensors can help resolve. For instance, when examining the structural integrity of a wind

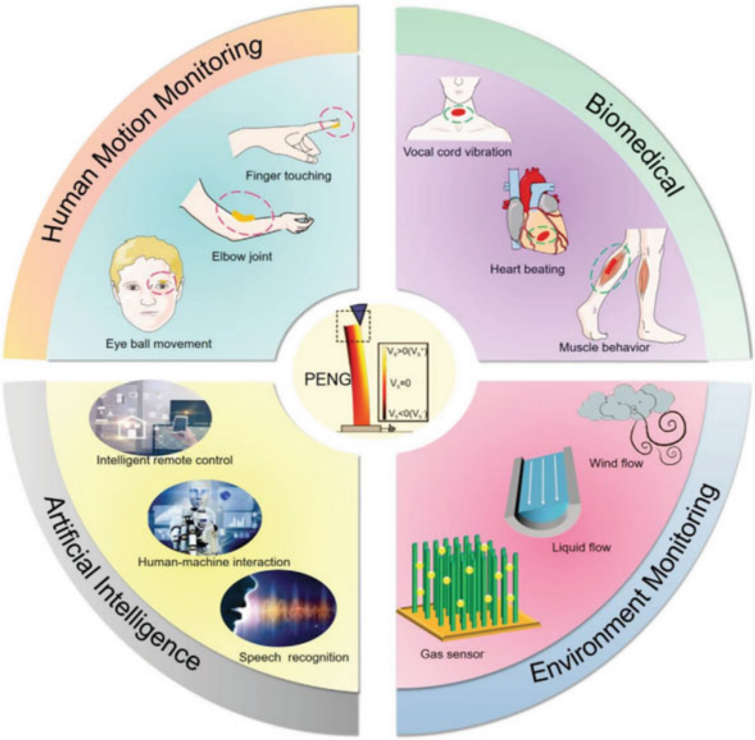

Fig. 9 Application of piezoelectric nanogenerator-based active self-powered sensors [85]. Copyright (2021) Wiley

turbine blade, big copper lead wires would frequently produce noisy data with electrical sensors. Wind turbine blade strain measurements can be performed with optical sensing with little additional weight to the structure [76]. Energy sources such as kinetic energy, wind, water, and solar energy are just a few examples of the numerous sustainable and environmentally friendly clean and renewable energy sources developed as alternatives to conventional fossil fuels. The reliability and cost of the power supply are adversely affected by environmental conditions, which substantially impact various energy sources. Although mechanical energy is standard energy in the environment, it is typically wasted in daily living, for example, vibrations, human movements, and fluid flows caused by wind and water.

8 Conclusion and Future Perspectives

In conclusion, this book chapter highlights the significant advancements and potential applications of metal–organic framework (MOF)-based optical fiber sensor (OFS) systems that incorporate ML algorithms and AI technologies. MOFs, with their unique combination of organic struts and metal ions/clusters, have emerged as intriguing porous materials with diverse properties and applications. The chapter discusses the advantages of MOFs, such as their large surface area, tunable pore metrics, and functional nano-spaces, which make them superior to contemporary alternatives for sensing various species. MOFs exhibit excellent sensing capabilities through signal transduction-induced processes in their nanogaps, enabling optical output that can be monitored using different methods. The chapter specifically focuses on luminescent MOFs (LMOFs) and their improved guest identification abilities, resulting in analyte-specific optical responses. Optical fiber sensor (OFS) configurations with redundancy and neural architecture-based ML models can serve as the foundation for constructing such solutions. Furthermore, improved ML and AI-based techniques can not only provide multiparametric detecting abilities but can also reduce the number of transducers required to achieve desired sensing objectives. While MOF-based sensors typically rely on luminescence quenching mechanisms, LMOFs offer selective analyte detection and turn-on responsive behavior, making them highly desirable. MOFs' high specific surface area, ultrahigh porosity, and tunable interior surface properties contribute to their extensive applications in purification, storage, catalysis, medication delivery, biomedicine, and chemical sensors and biosensors. Overall, this book chapter provides valuable insights into the development and applications of MOF-based optical nanosensors, particularly in the field of luminescence detection. Furthermore, it emphasizes the advantages of optical fiber sensors in various industries, including healthcare, chemistry, and telecommunications, where their reliability, robustness, and ability to measure a wide range of physical characteristics are highly valued.

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Metrological Traceability of Optical Sensor

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Abstract A concept of metrological evaluation of optical fiber grating and optical biosensors is presented to provide a reasonable analysis of their performance. Significant emphasis is given to the most typical parameters such as sensitivity (incorporating sensitivity to surface and volume), reaction or response time, resolution, specificity, reusability, measurement ambiguity, accuracy, precision, detection limit, robustness or stability, and reproducibility. A high degree of precision and metrological traceability is employed in the assessment. This work examines the difficulties of rapid on-site decision-making and real-time monitoring, and it analyzes potential methods to increase the effectiveness of the optical sensing method. Furthermore, recommendations for enhancing the optical sensing performance and its validation are addressed.

Keywords Optical fiber grating · Biosensor · Metrological traceability · Sensitivity · Specificity · Process analytical technology

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1 Introduction

Optical sensors have revolutionized everyday life for adults through their various applications in different sectors. These devices are capable of detecting changes in their source/environment and collecting signals, allowing reactions to be designed. The various kinds of sources such as light, temperature, movement, and pressure can be detected by numerous kinds of sensors and used in a multitude of applications [1]. Innovative optical sensor technologies are continuously being used to enhance lifestyles. Additionally, the development of an efficient detection method that can simultaneously determine multiple analytes of interest is essential for critical decisions relating to the treatment of ailments, drug and food product testing, pollution problems, explosives surveillance, criminal investigations, and several other biomedical, industrial, environmental and security concerns [2]. To increase the number of detectable analytes and enable the recognition by non-specific interactions, moving from single lock-and-key sensors to the optical sensor is essential [3]. Hence, optical sensors are extensively utilized in manufacturing, healthcare, automotive electronic systems, and safety equipment.

Optical-based sensors employ visible or ultraviolet light to measure the characteristics of a sensor [4]. Generally, they consist of a light source that can be tuned to a certain wavelength, the transducer material that interacts with the analytes, and a detector. Depending on the technique or principle employed such as scattering, refractive index, absorbance, reflectance, diffraction, chemiluminescence, and photoluminescence, a wide range of electromagnetic spectrum regions can be monitored, enabling the measurement of numerous attributes including light's intensity, longevity, and polarization [5]. Arrays of the optical sensor provide a significantly convenient, effective, and sensitive way to quickly detect and identify a variety of chemical compounds based on color or change in fluorescent that are analyzed by using digital imaging [6]. Each array must consist of a strong chromophore or fluorophore attached to a center that interacts firmly with analytes. It is the interaction between the analytes and the active center, frequently via an intense chemical reaction as compared to mere physical adsorption, which leads to color or fluorescence change, i.e., chemoresponsive [7]. Optical sensor technology has a wide range of applications across various fields. Some of the most common applications of optical sensors are:

(a) **Medical Sensing**

Optical sensors are widely used in the medical industry for various applications such as monitoring heart rate, blood pressure, oxygen levels, and glucose levels in patients. Moreover, they can also be used in imaging applications such as endoscopy and ophthalmology.

(b) **Environmental Monitoring**

To monitor various environmental parameters such as temperature, humidity [8, 9], gas concentrations [10–13], and water quality. They can also be used for monitoring air pollution levels in urban areas.

(c) **Industrial Sensor Technology**

Optical sensors are significantly employed in manufacturing and industrial processes to monitor parameters such as temperature, pressure, and strain. Broadly, it is also used for quality control in food and beverage processing and packaging.

(d) **Automotive Industries**

Various automotive applications such as anti-lock braking systems, airbag deployment, and tire pressure monitoring systems.

(e) **Security Sensing**

Optical sensors are utilized in surveillance cameras, motion detectors, and perimeter monitoring systems, among other security equipment.

(f) **Consumer Electronics**

Consumer devices like smartphones and tablets use optical sensors for several functions, including proximity sensing, ambient light sensing, and fingerprint sensing.

Overall, the applications of optical sensor technology are vast and diverse and continue to expand as new technologies are developed. Additionally, optical biosensors are classified into the different categories.

1.1 Optical Fiber Grating Sensor

Optical fiber grating sensors (OFGs) are diffractive structures that feature periodic changes in the Refractive Index (RI) in the Single-Mode Fiber (SMF) core [14]. These phase-match criteria are met for the cladding mode, core mode, and radiation mode (or perforated mode). Thanks to phase matching principle, fiber Bragg gratings (FBGs) and long period gratings (LPGs) enable the transfer of power between modes within an optical fiber, which is controlled and efficient. This results in the modulation of the transmitted spectrum. A grating's period range Λ is used to classify the different types of grating. An FBG grating has a grating period of hundreds of nanometers, which allows phase matching between the counter-propagating mode and its core mode. Due to these characteristics, when an optical broadband signal is received by the grating, only a small part of it is reflected, while the rest is transmitted [15]. The resonance wavelength (λ_{res}) at which the light is reflected satisfies the well-known Bragg equation.

$$\lambda_{res} = 2n_{core}^{eff}\Lambda \tag{1}$$

where n_{core}^{eff} has an effective RI, when used in core mode. This resonance peak has a spectral width of a few hundred picometers, which is dependent on the length of the grating. An FBG's basic operating principle is depicted in Fig. 1.

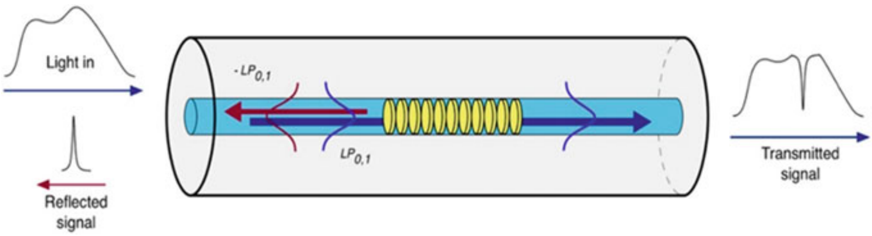

Fig. 1 An illustration of a uniform fiber Bragg grating coupled to its coupling mechanism [51]. Copyright (2017) MDPI

Optoelectronic and integrated optics devices are made with OFGs because they exhibited several advantageous properties such as miniaturized, small physical size, and lightweight [16]. Furthermore, these sensors are immune to radio-frequency and electromagnetic interferences, which are extremely compatible with optoelectronic devices and components and suitable for application in hazardous or hostile environments because due to their chemical and electrical inertness. Furthermore, since they are spectrally modulated, the signals are multiplexed and can be measured remotely.

1.2 OFG-Based Refractometer

The interactions between the fiber's evanescent field and the environment's interface are crucial for OFG-based refractometers. This field is produced by the interference of the incident and reflected rays, which results in an evanescent wave that travels down the fiber's axis and degrades exponentially perpendicular to the interface between the fiber and the environment as illustrated in Fig. 2a [17]. The evanescent field's penetration depth affects these platforms' sensitivity δp, that is a separation from the interface where the amplitude of the electric field has decreased to 1/e from its initial value. Generally, the amount of radiation in contact with the external medium increases as δp increases, which results in higher sensitivity. Since the δp is determined by the surrounding RI, coupled cladding mode, and operation wavelength, hence, the greater wavelength leads to the deeper the evanescent wave will penetrate the external medium [18].

As illustrated in Fig. 2b, it's important to recognize the distinction between a RI surface change and a bulk or volume RI change, which is the basis of an optical refractometer's ability to measure volume RI changes. By considering its importance for measuring surface refractive index (RI) changes that occur when a bioanalyte interacts with a sensing membrane fabricated on a fiber surface (here considered as a "biolayer"), the existence of biosensors is invaluable.

The adaptability of refractometers made with optical fibers has allowed for their use in identifying different types of heavy metal ions by selecting the proper surface coating. OFG refractometers were designed for the heavy metal group's usage to

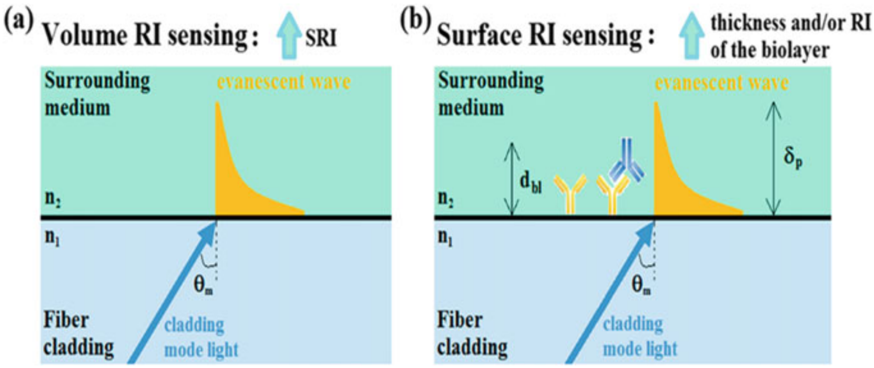

Fig. 2 **a** Illustration of a bulk or volume change is employed as an example of RI sensing. **b** A diagram of the RI sensing method relying on surface alteration, where just a fraction of the evanescent wave interacts with the biolayer, is presented (Bio-layer thickness d_{bl} < evanescent field penetration depth δp). n_1: RI of fiber cladding (generally considers as denser medium RI); n_2: RI of the surrounding medium (or typically the RI corresponding to the less dense medium); δp: penetration depth of evanescent field; d_{bl}: thickness of bio-layer

identify Ni^{+2}, Pb^{+2}, Cu^{+2}, Fe^{+2}, Cd, Co^{+2}, and Hg^{+2} ions [19]. In the context of employing the OFG refractometer as a biochemical sensor, the TIGF refractometer was also used for the detection of human leukemia cancer cells [20], urinary protein [21], and glucose monitoring [22].

1.3 Fiber Optical Chemical Sensors

The initial purpose of fiber optic sensors (FOS) was to assess physical characteristics including acceleration, strain, temperature, and position by detecting changes in light transmission caused by alterations in a medium being sensed. Recently, however, interest in using fiber optics to measure chemical properties has been increasing, resulting in the creation of a fiber optic chemical sensor (FOCS) [23]. These devices are now in use around the world, with more and more people turning their attention to this technology. FOCS can be categorized into two different groups, namely, extrinsic and intrinsic FOCS. Extrinsic FOCS employed indirect sensing of an analyte by detecting an optically detectable alteration in an immobilized indicator which is present at the fiber end. However, intrinsic FOCS features that the analyte and light interact directly, making use of the fiber itself in the sensing process. This interaction alters the optical characteristics of the fiber, such as absorption, emission, refractive index, and polarization, which are then used to measure several kinds of biochemical analytes.

The FOCS method is rapidly growing in popularity due to its numerous uses in a variety of fields including environmental, agricultural, chemical (both organic and inorganic), forensic, pharmacological analysis, and biotechnological control involving an intrinsic color or fluorescence.

The FOCS sensors demonstrated the following characteristics [24, 25].

- Highly sensitive.
- Selective.
- Continuous and reversible processes can both be used, or either of them can be chosen independently.
- Quick response.
- The experiment remained consistent throughout.
- The remote sensing system should be responsive so that it can detect a variety of analytes without requiring different sensing methods for each one.

1.4 Fiber Optical Biosensor (FOBS)

A fiber optic sensor is an example of a waveguide that takes advantage of the total internal reflection (TIR) concept, in order to accompany the light through its cylindrical core [26]. Depending upon the number of modes that pass through it, the FOBS has been categorized into two types: single-mode fiber (SMF) and multi-mode fiber (MMF). The core of an SMF has a diameter of only 8–10 μm and only allows one mode to travel. On the other hand, MMF has a larger core diameter (50–100 μm) that allows multiple modes to propagate. Generally, FOBS exhibited a metallic thin film or nanostructure (typically thickness in the nm range) together with the sensing area to evoke the surface plasmon resonance phenomena (SPR) or localized surface plasmon resonance (LSPR) [27, 28]. In order to identify a specific target, sensing membrane interfaces are stabilized by using various antibodies, proteins, DNA, or other sensing materials. The detection mechanism based on either SPR or LSPR effect, wherein the cladding region is occupied by the evanescent field and further interacts with the fabricated thin layer of metals, can be excited [29, 30]. After many years of extensive research, various optical fiber sensing configurations have been developed for real-time biosensing applications. The hetero-core design in particular has been successfully applied for G protein and RI sensing.

The summary of previously reported optical sensor applications has been depicted in Table 1.

2 Importance of Metrological Traceability

Metrological traceability can be defined as "the ability to trace the result of a measurement or measurement standard value as compared to a predefined stated reference, typically an international or national standard, through a continuous series of comparisons with specified uncertainties" [39]. It is essential to have metrological traceability to ensure consistent measurement results in different spaces and times. In

Table 1 Literature review of the various optical-based sensor applications

Sensing principle	Analyte	Sensitivity	LOD	References
Fiber grating	Glucose	1.33 nm/mg/ml	0.4 mg/ml	[31]
Fiber grating	Glucose	12.211 nm/mg/ml	0.4 mg/ml	[32]
Fiber grating	pH	0.41 nm/pH	–	[33]
Fiber grating	Ni^{+2}	40.52 dB/mM	–	[34]
Fiber grating	Cd^{2+}	230 dB/RIU	–	[35]
Tilted fiber grating	Pb^{+2}	0.5 × 10–3 dB/ppb	–	[36]
LPG-based interferometer	Salinity	6.61 pm/(g/l)	–	[37]
MMF-SMF	Glucose	0.0267 nm/mg/ml	<3.4% (0.189 M)	[38]

addition, the international acceptance of metrological traceability for stated references, along with their declared measurement uncertainties, provides the foundation for reproducibility and comparability of the many measurements related to sensors and sensing systems [40]. To illustrate the importance of this, some examples can be given. In the environmental field, metrological traceability is crucial to accurately determine the concentrations of pollutants or contamination in soil, air, and water, so that compliance with environmental regulations can be accurately assessed and appropriate measures are taken when necessary [41]. Similarly, the number of impurities, hazardous residues, and preservative additives in foodstuffs must be precisely determined to prevent the health of consumers [42]. Metrological traceability in the field of bioscience can be of immense value in assuring accurate results from clinical tests. Measurement uncertainty provides insight into the quality of results and can determine whether the range of values associated with a physiological property is adequate for the corresponding clinical diagnosis [40]. The estimate of uncertainty can evaluate the dispersion of results to meet the precision needed for diagnostics and supply physicians with important data for better decisions and more appropriate treatments. Accuracy is crucial when it comes to the use of the optical sensor for biomedical diagnostics in medical laboratory results (laboratory medicine) to ensure welfare and effectiveness in medical diagnosis and therapies [43]. The same thing occurs in forensics anytime findings are presented as evidence in court, as well as in sports when evaluating compliance with anti-doping regulations. Finally, it is critical to minimize technological trade obstacles by using precise and trustworthy measures. The importance of metrological traceability is highly required in various kinds of applications, for example, in-vitro diagnostic (IVD) products require effective and accurate results to improve the quality of health care. In this context, IVD-based organizations can establish a dependable transfer of the accuracy of measurements from the topmost tier of the metrological hierarchy to the calibration instruments of commercial methods utilized in clinical laboratories. Hence, manufacturers of IVD medical devices must ensure the traceability of their analytical systems to recognize higher-order references in compliance with the EU

Directive 98/78, which is supported by two specific ISO standards [44]. Furthermore, concerning the oceanic ecosystem, the degree of CO_2 (measured through its partial pressure, pCO_2) in seawater is a crucial component of climate analysis. This measurement can be taken through the implementation of networked sensors. At a continental scale, the "Marine Strategy Framework Directive 2008/56/EC" mandates the establishment of standardized methodologies for evaluating the condition of the marine environment, as well as for its consistent monitoring and the achievement of environmental goals [45]. The ISO/IEC 17025:2005 criterion applies to laboratories that engage in testing and calibration, intending to prove their technical proficiency and management system efficiency. The standard's technical specifications rest on metrological traceability for both testing and calibration. However, medical (clinical) laboratories should utilize the ISO 15189:2012 standard [46].

3 Metrological Traceability of an Optical Sensor

Optical sensors have exhibited several advantages and drawbacks. These sensors are advantageous due to their small size and weight, making them sufficient for the mass manufacturing of optoelectronic devices. Also, the optical sensor device exhibited a substantial amount of remote monitoring abilities, minimal transmission decay, excellent resistance to corrosion, natural electrical insulation, and resistance to electromagnetic disturbance. However, optical sensors exhibited some disadvantages of being sensitive to multiple factors simultaneously, such as humidity, pressure, temperature, RI of the medium, and axial deformation (i.e., strain). The scientific community is paying increasingly more attention to optical sensors, making a worldwide accepted standard for their sensing performance benefits to both research and industrial communities [47]. Hence, to evaluate the accuracy or the typical optical sensor efficiency and robustness, the principle of metrological traceability that is commonly associated with sensor terminology needs to be understood.

In 2001, one of the earliest attempts was tried to create a standardized set of "fundamental explanations of sensor characteristics" for researchers and scientists. They described the analysis of sensor performance by examining the sensitivity, responsivity curve, signal-to-noise ratio, drift, hysteresis, selectivity, and resolution as a common practice [47]. These parameters provide an understanding of the sensor's ability to accurately detect and measure a given input. In 2008, the further evaluation focused on the minimum limit of detection (LOD) and the impact of the quality factor (Q-factor) for resonance-based RI optical sensors. Moreover, to better concentrate on other standardization parameters for FOCS or FOBS, the International Organization for Standardization (ISO) utilizes the Minimum Detectable Concentration (MDC) while the International Union of Pure and Applied Chemistry (IUPAC) employs the LOD [48]. Assessing the performance of sensors requires considering both their compelling features and capabilities. In "Recommendations for the design of optical resonator biochemical sensors", the significance of using a generally acknowledged figure of merit (FOM) to contrast various technology platforms was emphasized.

The RI-based sensor LOD and Q-factor, which are significantly impacted by the full width at half maximum (FWHM) of resonance peak, were identified as key metrics for this purpose [49]. In the case of OFG sensors, repeatability and reproducibility are the main sources of uncertainty. It is attributed to the combined effects of OFG cross-sensitivity and environmental conditions, resulting in the need for some compensation procedures and more measurements. Metrological parameters for optical fiber sensors can be categorized into two main types: optical refractometers and optical biosensors. Optical refractometers measure sensor RI which changes as a function of the entire volume surrounding the sensor, referred to as bulk RI or volume RI. When it comes to optical biosensors, surface RI measurements involve only the sensing surface of the sensor where the target specifically interacts [50].

4 Assessment of Optical Sensor Performance with Metrological Traceability Parameters

This section outlines the different metrological parameters, which mostly used in optical sensing, particularly those relevant to OFGs. Three subsections are outlined as (1) parameters of generic interest applicable for physical optical sensors, (2) parameters associated with volume RI sensing, (3) parameters related to biosensors.

4.1 Parameters of Generic Interest

Every type of sensor has a range of parameters of general interest that should be taken into consideration. These parameters include accuracy and precision, uncertainty, sensor drift, response time, repeatability or reproducibility, which are described in the following subsections. The sensor datasheet should include these parameters if a commercial device is implemented.

4.2 Accuracy and Precision

There is a common misconception about accuracy and precision. Accuracy measures the difference between the average value obtained from a set of measurements and the true value of the measurement taken as the reference. It indicates how close the measurement is to the real value. However, on other hand, precision measures the level of variation (or variance, σ^2) around the mean value. It shows how each individual measurement compares to the other. Measuring can generally be done accurately, precisely, and accurately, or neither accurately nor precisely.

4.3 Uncertainty

It is essential to state the uncertainty (which means a margin of error) of any measurement in metrology. The uncertainty gives an interval of values that are likely close to the true amount of the measurement, and can be seen in a graphical representation through the error bar or the symbol of "measured value ± uncertainty". Calculating the standard deviation (σ) from multiple readings will provide an uncertainty measurement. A single reading has an uncertainty of σ. The uncertainty, however, is reduced to the standard error of the mean by averaging the measurements. This is equal to the standard deviation divided by the square root of the number of measurements, $\sigma/\sqrt{n}$.

4.4 Sensor Drift

The fluctuation, as well as the drift of a sensor, are two essential factors that are sometimes disregarded yet are deserving of more consideration since it decides the level of stability of an optical sensor for a short or longer period. As a matter of fact, stabilizing environmental parameters is the first step. It is evident that the primary step is to stabilize environmental parameters like humidity, temperature, potential strain, etc. Different kinds of tests can be conducted to determine a product's stability by measuring how the resonance wavelength (λ_{res}) changes over time under a specific environment (e.g., 20 °C in the air). However, the degree of drift can be determined from the results of the stability test if a distinct pattern is observed during the experiment.

Figure 3 presents the outcome of a long-term stability assessment conducted with different comparable LPGs in distinct environmental settings. The device was positioned within a temperature-controlled microfluidic system at a predefined temperature of 23 ºC (Fig. 3a), while the other device was placed in an open cell under below-controlled laboratory conditions (Fig. 3b). The drift value on λ_{res} (red curve) was initially 0.2 pm h^{-1} (considerably stable), with a temperature deviation of ±0.03 ºC (shown in blue curve). However, in the other case, the obtained drift value on λ_{res} was markedly higher at 17.3 pm h^{-1}, accompanied by a temperature deviation of ±0.5 ºC (a magnitude greater than before) [51].

4.5 Response Time

The response time of an optical sensor is the time it takes for the sensor to detect a change in light intensity and produce a corresponding output signal. This response time can vary depending on the type of sensor and the specific application. Generally, optical sensors have a fast response time due to the high speed of light. For example,

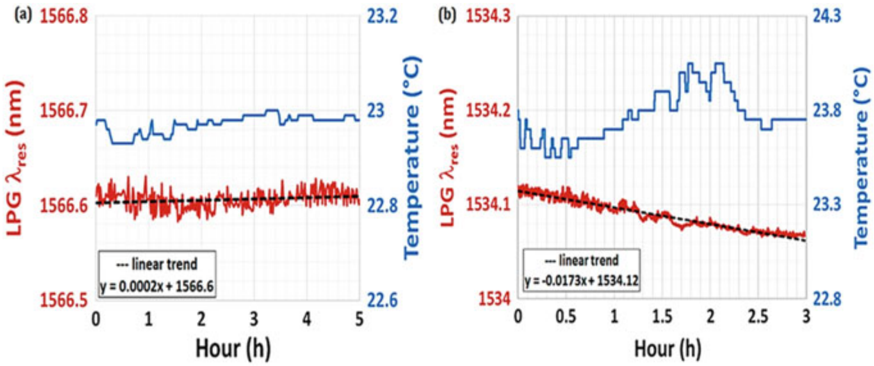

Fig. 3 **a** A thermostabilized microfluidic device was used to conduct a long-term accuracy performance by employing a standard LPG at a predetermined temperature of 23 °C. **b** In a controlled lab environment, another LPG was found in an open cell. Thermal alterations during the experiment are depicted by the blue curves. With the black dashed lines illustrating the sensor drift, the red curve line depicts the time evolution of λ_{res} [51]. Copyright (2017) MDPI

a typical photodiode can have a response time on the order of nanoseconds (10^{-9} s), while more advanced sensors like avalanche photodiodes can have response times on the order of picoseconds (10^{-12} s). However, the overall response time of an optical sensor can also be affected by other factors such as the circuitry used to process the output signal and the presence of noise or interference. As such, it is important to carefully consider the specific requirements of a given application when selecting an optical sensor with the appropriate response time.

4.6 Repeatability

Repeatability is the degree of consistency between multiple measurements of a particular value, using the same device and under the same conditions. A sensor's lifespan and stability are significantly determined by this test. An error in the repeatability test majorly affects the accuracy and is the minimum limit that can be achieved when taking the measurements. Based on the measurement unit, the repeatability data is usually expressed in percentages.

5 Parameters Associated with Volume RI Sensing

The parameters primarily connected to devices that depend on volume RI sensing will be the subject of this initial section's attention.

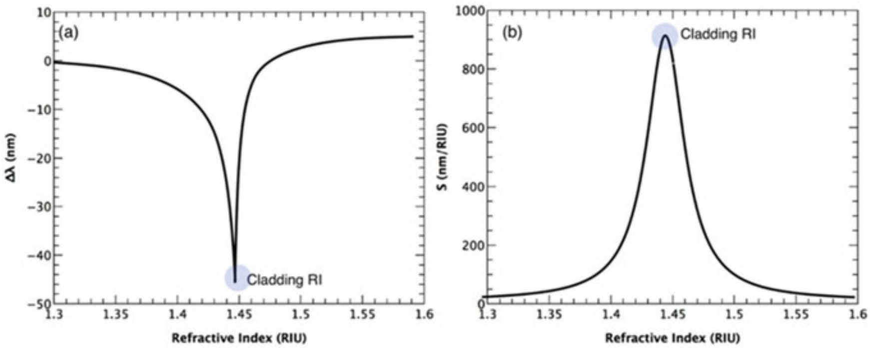

Fig. 4 **a** An example of a bare LPG's typical reaction curve to the SRI in the 1.30–1.60 range with its corresponding sensitivity. **b** In the SRI region near n_{clad}, a non-linear pattern is observed with a rising sensitivity [51]. Copyright (2017) MDPI

5.1 Response Curve and RI Sensitivity

Sensor responses to different SRIs can be determined by examining the resonance wavelength (λ_{res}) of an OFG sensor. An experimental point (mean value) is generated by calculating the average λ_{res} within a specific time or the measurement numbers, with its corresponding standard deviation acting as an error bar. The sensitivity parameter (S) of the OFG sensor is then expressed as the derivative of the response curve ($\partial\lambda_{res}/\partial n_{sur}$), given in nm/RIU. Figure 4a displays a typical LPG response curve and Fig. 4b depicts the LPG's relationship between the SRI and sensitivity of the SRI.

5.2 Resolution

The minimal increment in the SRI that a sensing device can detect is referred to as Resolution. This is equal to the amount of SRI needed to cause a detectable alteration in λ_{res}. This is inversely proportional to the sensitivity of the sensor volume.

$$R = \frac{p\sigma}{\mathrm{S}} \tag{2}$$

σ is determined by examining multiple measurements in consistent and repeatable circumstances (which includes all sources of noise) and p represents the confidence level considered. It is common to calculate R by simply dividing the instrument's spectral resolution by the sensor's sensitivity.

6 Parameters Associated with Optical Biosensor

A detailed description of optical biosensor parameters is included in this section such as sensitivity, calibration curve, limit of detection (LOD), selectivity, and reusability are significantly explained.

6.1 Sensitivity

Sensitivity refers to the ability of an optical sensor to detect and respond to changes in the amount of light or other optical signals it receives. It is measured by the ratio of the output signal of the sensor to the input optical power or signal level. A highly sensitive sensor produces a larger output signal for a given input signal, making it more adept at detecting small changes. The sensitivity of an optical sensor is influenced by factors such as the sensor design, materials used, and wavelength of the input signal. Additionally, external factors like temperature, noise, or interference can also influence the sensor's sensitivity. High sensitivity is crucial for optical sensing applications that require high accuracy or the detection of weak optical signals.

6.2 Calibration Curve

It is a graph that represents a calibration curve that illustrates the signal alteration in relation to the concentration of the analyte being studied, as shown in Fig. 5. In the case of OFG, the curve displays the deviation or change in the λ_{res} as the concentration of the analyte increases and represented in either logarithmic or linear scale. This signal can be shown as either the absolute value or the shift of λ_{res} scaled to the reference concentration, which is the concentration at zero analytes, referred to as the blank measurement. The experimental points and fitted curves should be in excellent agreement, as shown by the correlation coefficient (R^2), which is equal or more than 0.999 [52].

6.3 Limit of Detection (LOD)

The LOD is an essential measure of biosensor performance, which expresses the concentration (C) of the analyte being studied in terms of g L^{-1} (often in terms of μg/l or ng/l, taking the analyte molecular weight into account), or molarity (M). The determination of LOD relies on the utilization of a calibration curve of biosensors, On the other hand, the LOD can be calculated by taking three times the standard deviation of the blank measurement, according to the IUPAC (3σblank) [53].

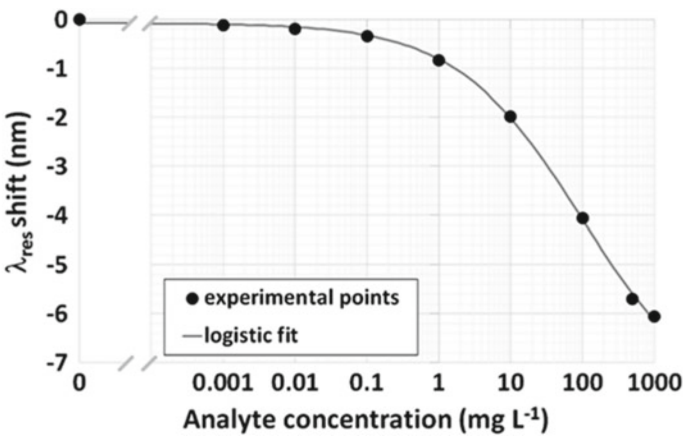

Fig. 5 An illustration of a calibration curve for a biosensor based on LPG with analyte spiked in serum matrix [51]. Copyright (2017) MDPI

6.4 Specificity or Selectivity

Selectivity and specificity are critical factors in any sensor but they are especially essential for chemical and/or biochemical optical sensors. Selectivity is the sensor's capacity to recognize a particular measurement, as opposed to any other interfering analyte, often referred to as cross-sensitivity. It is challenging to develop a sensor that is only specific to one measurement [54]. In this regard, it is important to note that the parameter called selectivity is more commonly used for chemical sensors, gas sensors, electronic tongues, and e-noses, while the specificity is mainly associated with optical-based sensing devices. The specificity of a biosensor can be tested by measuring its sensitivity to a particular target analyte when it is added to a solution containing only that analyte. To further evaluate the biosensor's specificity, a negative control can be used, which is a solution containing different analytes than the one being tested.

6.5 Reusability or Regeneration

Reusability and regeneration of the sensor are an integral part of biosensing, opening up possibilities for real-world applications. The integration of systems makes it possible to design an assay protocol that involves regeneration at the end of each cycle, allowing the specific biolayer to be used multiple times, instead of just once [55]. To evaluate the effectiveness of the reusability of the sensor, a standard protocol involves measuring the same concentration of an analyte three times after each regeneration cycle [56]. The initial step of reusability entails selecting the optimal regeneration solution based on the analyte/bioreceptor pair. The same regeneration solution may be highly effective for a particular analyte/bioreceptor pair, however, not for any others. In order to assess the effectiveness of regeneration, a standard and predefined procedure includes measuring the same analyte concentration after each regeneration cycle—a minimum of three times.

6.6 Recovery Time

An optical sensor's recovery time refers to the duration it takes for the sensor to return to its original state after being exposed to a stimulus. When an optical sensor detects a sudden increase in light intensity, it may require some time to adjust and return to its baseline sensitivity. The recovery time of an optical sensor can vary greatly, ranging from microseconds up to several seconds, depending on the particular sensor and its operating conditions. In high-speed applications such as telecommunications or data transmission, faster recovery times are often preferred to minimize signal distortion and maximize data throughput. It is worth mentioning that recovery time is just one of several key performance metrics used to evaluate the effectiveness of optical sensors.

6.7 Operating Temperature

When choosing an optical sensor for a specific application, it is crucial to take into account its operating temperature range. It is necessary to ensure that the sensor can function reliably within the prescribed temperature range, while also minimizing any temperature-related performance problems, including thermal drift or sensitivity changes. In some instances, like fiber optic communications, the operating temperature range of certain optical sensors may be narrow, normally ranging from -40 °C to $+85$ °C. This temperature range is generally satisfactory for most telecommunications applications, but it may not be adequate for high-temperature conditions, such as those found in industrial or aerospace settings.

7 Requirement of Metrological Traceability for Implementing Optical Sensor

In the context of optical sensors, metrological traceability is important for ensuring the accuracy and reliability of measurements made with these devices. To establish metrological traceability for optical sensors, the following steps can be taken:

(a) **Calibration**: Optical sensors should be calibrated using a traceable standard such as a National Metrology Institute (NMI) certified reference material or reference instrument.
(b) **Verification**: The calibration process should be verified to ensure that it meets the required measurement uncertainty and that the calibration is consistent over time.
(c) **Documentation**: The calibration process should be documented in a calibration certificate, which should include the details of the calibration standard used, the calibration procedure, the measurement uncertainty, and any other relevant information.
(d) **Accreditation**: Calibration laboratories can be accredited by an internationally recognized accreditation body, such as the International Organization for Standardization (ISO), to demonstrate that they meet specific standards for calibration and measurement.
(e) **Chain of traceability**: The calibration laboratory should be able to demonstrate a clear chain of traceability from the reference standard to the calibration certificate, and ultimately to the measurement made with the optical sensor.

Establishing metrological traceability for optical sensors ensures that measurements made with these devices are accurate and reliable and can be compared with measurements made using other traceable instruments. This is important for ensuring consistency in measurements across different laboratories and for promoting international trade. Many international organizations and committees, including the ISO and the European Committee for Standardization (CEN), are working to enhance the uniformity of optical biosensor results across laboratories. In this instance, according to Soriano et al., analytical reliability should be utilized as a general characteristic for procedures that produce conventional qualitative and quantitative results, complete indices, and method-defined parameters, as shown in Fig. 6 [57]. This is a measurement that can only be acquired by utilizing an established optical and biochemical detection measurement process. Also, it is recommended that reliability studies be incorporated into the initial stages of the validation process due to the value they contribute to the definition of an analytical method in terms of the caliber of the analytical data and the requirements of the user.

Manufacturers of optical sensor devices are responsible for validating and testing their performance to ensure they are suitable for their intended use, unless they are used by qualified laboratories, they cannot be further used. For the validation and verification of the applicability of methods in real-world situations, the scientific community and technology developers must follow standard procedures. To ensure their suitability for the purpose, the accuracy and metrological support of optical sensor devices and process analytical technologies analyzers (PAT) for real-time and point-of-care analysis, particularly commercial ones, should be weighed against their advantages in terms of speed, affordability, and ease of use, as depicted in Fig. 7 [58]. This balance is often neglected as the scientific community mainly focus on innovative and novel methodology without providing sufficient data based on their

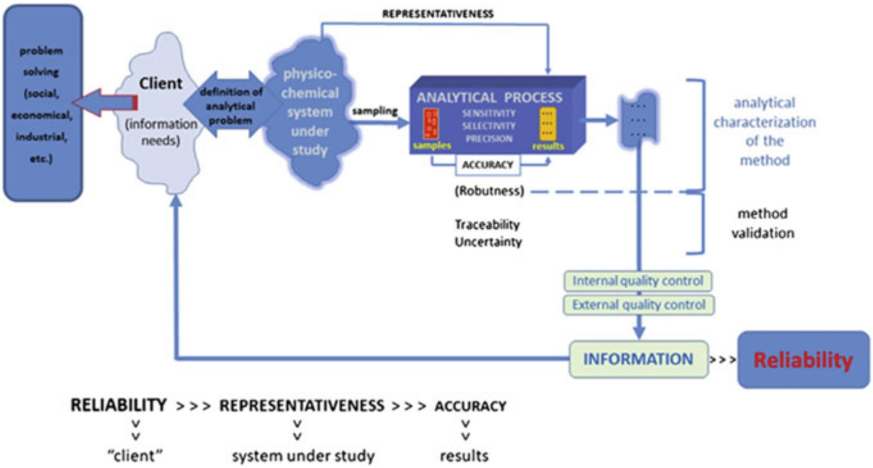

Fig. 6 Examining the relationship between analytical data and the client's desired outcomes at various levels of hierarchy [58]. Copyright (2022) Springer Nature

attributes of performance to determine the accuracy and validity of the analytical data for the intended utilization.

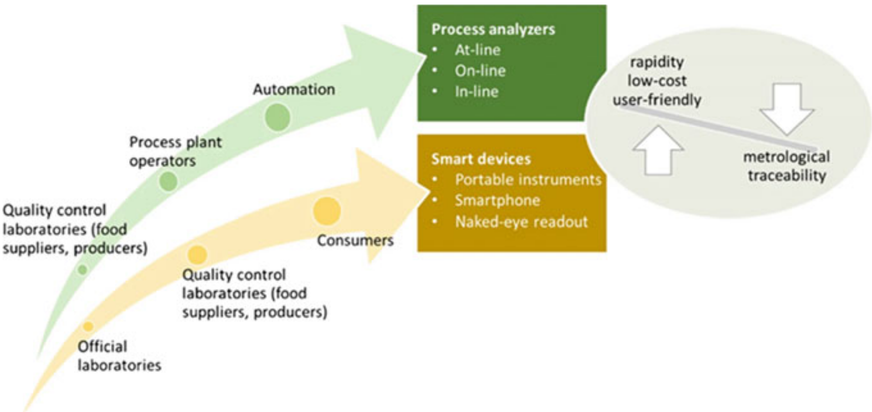

Fig. 7 Maintaining the equilibrium between the expected performance of Process Analytical Technology (PAT) and optical sensors, as well as metrological traceability [58]. Copyright (2022) Springer Nature

8 Conclusion

This chapter explores the developing considerations concerning the metrological traceability application in the specific area of optical sensors such as imaging, remote sensing satellite, metrology, medical devices, and quality and process control. It also broadly examines the technical parameters such as sensitivity, calibration data, accuracy, response time, and repeatability of the global regulatory framework for the assurance of reliability, safety, and performance of sensor technologies. It is impossible to overestimate the significance of metrological traceability for assuring the comparability of analytical data, and device manufacturers and researchers must pay close attention if PAT strategy measurement results are to be trusted. This necessitates a critical assessment of optical sensor performance characteristics.

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Optical Sensors Based on Polymeric Materials

Shital J. Shinde, Maqsood R. Waikar, Rakesh K. Sonker, and Rajendra G. Sonkawade

Abstract Modern sensor devices use polymers as essential components. For sensors, conductive polymers (CPs) offer a variety of benefits including high sensitivity, rapid reaction times, room temperature functioning, and the ability to tailor both chemical and physical properties by utilising various substituents. Because of this, researchers have given CP-based sensors and their composites a lot of attention. The primary components of the CPs utilised for sensors are poly (3,4-ethylenedioxythiophene), polypyrrole, polyaniline, etc. Polymer technology is a fastest-growing science in modern science due to its ability to assemble polymer networks with well-defined structures using a wide range of synthetic chemical routes to produce materials with extraordinary macroscopic properties. There are several types of optical sensors that have been created including colorimetric, electrochemiluminescence, fluorescence, and surface plasmon resonance ones. An optical sensor that measures changes in the colour of an indicator is a colorimetric sensor. The various polymer synthesis methods will be explained in this book chapter. The applications for polymer-based sensors such as all-flexible sensors, highly sensitive sensors, solid-state sensors, highly selective sensors and stretchable sensors will be explained in detail. In this book chapter novel synthetic methods, CP derivatives, and their conjugates for sensors have been studied to explain the mechanism of sensors in more detail.

Keywords Polymer · Conducting polymer · Sensor devices

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1 Introduction

During the course of more than a hundred million years, the light is employed to detect environmental changes or unusual purposes. The optical sensor method was developed many hundred years ago [1]. Since decades, the field of optical sensors and optodes has become crucial [2]. Due to their numerous uses in biotechnology, ecology, and medicine, optical sensors require significant improvement. Optical sensors have a number of benefits including low cost, little electrical interference, safety, and the potential for distant sensing. Applications for the optical sensor include temperature, pH and heavy metal ion detection. High sensitivity, low detection limit, good target-analyte selectivity, wide dynamic range, minimal calibration, fast response, repeatability, reversibility and stability are just some of the characteristics that an excellent sensor must meet [3]. Figure 1 summarizes and compares the merits and demerits of optical sensors for heavy metal ion detection [3].

Conducting polymers heralds the dawn of a new era in polymer development (CPs). The light weight, processability, corrosion resistance, affordability, and exceptional electrical, mechanical, and optical properties of CPs are only a few of its many attributes. CPs have been widely used in sensing applications due to their simple synthesis, wide detection range of volatiles, and excellent sensitivity. When CPs come into contact with the analyte, various changes occur such as solvation effects in the polymer chain, changes in spin conformation, attraction of impurity counterions or electron transfer [4]. Many materials including graphene oxide, polymers, and quantum dots are applied to optical sensors to enhance sensitivity and selectivity [3]. Polymeric materials can undergo reversible or irreversible changes in their physical

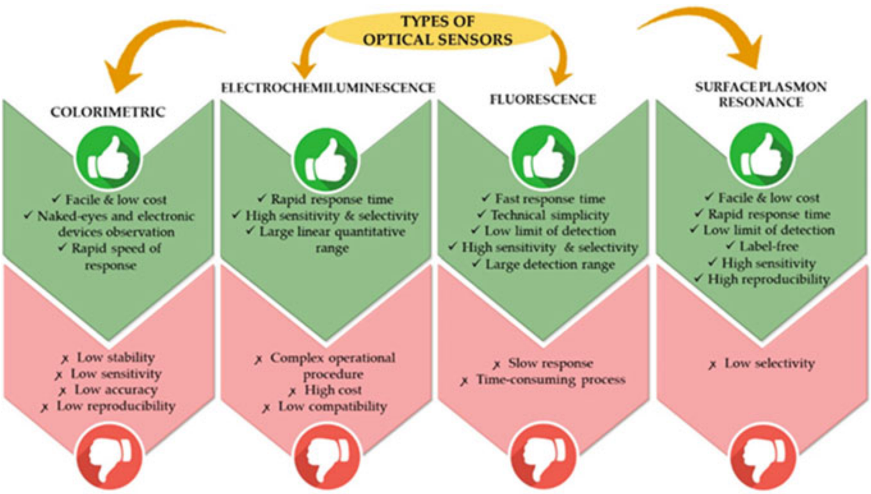

Fig. 1 Comparison of optical sensors' benefits and drawbacks for detecting heavy metal ions [3]. Copyright (2019) Elsevier

and chemical properties in response to external stimuli including pH, temperature, presence of certain ions, light radiation, mechanical forces, magnetic fields, electric fields, and bioactive compounds [5, 6].

Functional materials are currently evolving swiftly as a result of the emergence of cutting-edge technologies that demand the delivery of extremely complex feature combinations that polymers alone cannot provide [7]. Researchers have studied polymer composites containing colloidal crystals with lattice spacing higher than 100 nm, which diffract visible light in accordance with Bragg's law for use in optical sensor applications. In industry and for people's comfort humidity and gas detection are becoming more and more important. Governments all over the world are currently considering researching alternate renewable energy sources due to the consumption of non-renewable resources of fossil fuels like coal, oil, and natural gas, not only the ensuing effects on the environment but also human health caused by their combustion [8]. Researchers from all around the world have given humidity monitoring a lot of attention and created a number of sensing modalities for measuring relative humidity (RH) in terms of electrical or optical factors. As it affects practically all environmental phenomena such as humidity has grown to be of utmost importance. According to the literature, humidity sensors are crucial in a number of industries and professions including agriculture, construction, and health monitoring. They are significantly enhancing people's quality of life. An effective humidity sensor should be affordable, highly sensitive, stable over the long term, have quick reaction and recovery times, and have a wide operating range [9]. Food safety, environmental monitoring, and diagnostic applications can all benefit from using paper-based sensors. Moreover the construction of miniature analytical systems is made possible by nanomaterials. Yet, the potential for optical (bio)sensing applications of bacterial nanopaper has hardly been investigated too far [10].

Cadmium oxide (CdO) a transparent conducting material, is an n-type semiconducting material with a bandgap between 2.2 and 2.7 eV. From the perspective of applications for usage in opto-electronic and photovoltaic devices the material is very intriguing. For a variety of potential uses in contemporary technology such as photodiodes, sensors, flat-panel displays, solar cells, and optical communication, thin films of CdO are appealing components [11]. Sample sheets placed on a heater in a specially designed gas flow cell were used to measure optical absorbance and transmittance in order to test the performance of optical sensors in the 350 to 800 nm wavelength range. Transmission data were gathered for exposure to various CO concentrations in dry air using a Varian Cary1E spectrophotometer while the films were heated to T = 330 °C (working temperature). The incident spectrophotometer beam spanned a section area of 6 mm by 1.5 mm on a substrate that was approximately 1 cm by 2 cm for these measurements [12]. The specially built chamber was an aluminium box with openings for light, electrical hook-ups for a heating plate, and apertures for a gas input and outflow (Fig. 2 illustrates the schematic illustration). A deuterium-halogen single beam light source (Micropack DH200) was used to provide the optical signal and a spectrophotometer was used to measure it (Ocean Optics HR 4000). The sensing components were mounted on a specially made sample holder throughout the testing. These sensor devices functioning temperatures were

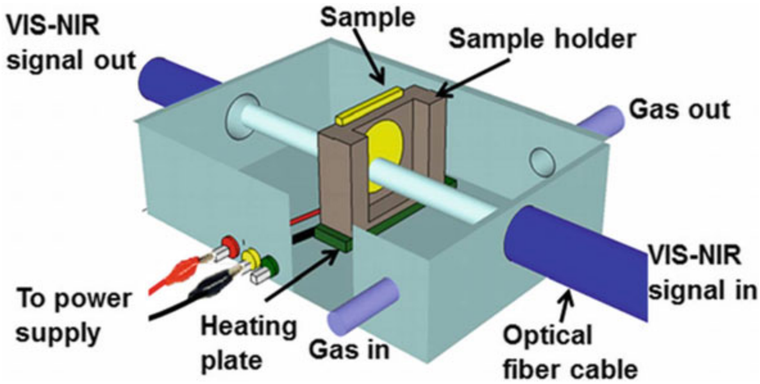

Fig. 2 Schematic illustration of the optical gas testing chamber [84]. Copyright (2015) American Chemical Society

controlled through a tiny heater attached to a dc power source. This chapter studies various polymerization processes, optical sensors, polymers, and composite polymer materials.

2 Types of Polymerizations

There are numerous methods for preparing polymers. A chemically stable monomer is transformed into a more stable polymer by the exothermic process of polymerization after specific amounts of energy have been lost. There are three different categories for polymerizations: addition polymerization, condensation polymerization, and metathesis polymerization [13]. This is explained briefly as follows.

2.1 Addition Polymerization

There is no loss of small molecules during the synthesis of the addition polymers from monomers. Olefins, acetylenes, and aldehydes are the unsaturated monomers. These monomers undergo addition polymerization [13]. Chain growth polymerization is another name for this process. The reactions occur in stages. At 8–20 kcal/mol of energy, the process is exothermic. The polymer transforms the monomers bond into a sigma bond. High molecular weight polymer is created during this polymerization. The most frequent and thermodynamically favourable chemical changes of olefins are the greatest illustration of addition polymerization. These polymers can be made by polymerizing them in bulk, solution, suspension, or emulsion. Monomers with two double bonds can be used to create cross-links. The addition type polymers are a common form of thermoplastic.

2.2 Condensation Polymerization

Water, ammonia, methanol, and HCl are just a few examples of the tiny molecules that might be dropped during the condensation polymerization process to bring two distinct monomers together. Step-growth polymerization is another name for it. The quantity of functional end groups affects the kind of condensation polymerization that results in the end product. Condensation polymerization uses monomers different from addition polymerization, which uses different monomers. The monomers are distinguished by two key features, such as the presence of functional groups such as –OH, –NH, or –COOH in place of double bonds. At least two reactive sites are displayed by monomers, which is another feature. The high molecular weight can be produced with this method at high conversion rates. Intensive ΔE_a was needed for condensation polymerization.

This is the indirect heating that is needed. If a monomer participating in this polymerization has just one reactive group, it will stop the chain from expanding and produce an end product with a lower molecular weight. Two reactive end-group monomers are used to create the linear polymers. Nevertheless, polymers that are cross-linked and three-dimensional are produced by monomers with more than two reactive groups. The linking of the monomer with a –OH group and a readily ionisable –H on each side was required for polymer dehydration synthesis. Two or more distinct monomers can cause this reaction to continue [13].

Polyester is synthesised by forming ester linkages between monomers, which include functional groups like carboxyl and hydroxyl. Diamines and carboxyl derivatives are combined in a condensation polymerization process to create nylon. Condensation polymerization is another method used to create proteins from amino acid monomers.

2.3 Metathesis Polymerization

The process of breaking and statistically rearranging an olefin’s carbon–carbon double bond to generate a polymer is known as “olefin metathesis.” Metathesis polymerization retains the carbon–carbon double bond in the polymer backbone chain, unlike conventional polymerization techniques that eliminate it. In the olefin metathesis reaction, the intermediate metallocyclobutane is produced by a cycloaddition reaction between the transition metal alkylidene complex and the olefin. Then, this metallocycle fragments in the opposite direction, resulting in the production of a new alkylidene and olefin. An equilibrium blend of olefins will eventually be produced if this process is repeated [13].

There are two different kinds of metathesis polymerization as mentioned below.

2.3.1 Acyclic Diene Metathesis (ADMET) Polymerization

When an acyclic diene like 1,5-hexadiene is used as the starting material for this kind of polymerization, ethylene is produced as a byproduct in the polymer while a double bond forms in the backbone chain.

2.3.2 Ring-Opening Metathesis Polymerization (ROMP)

Starting with a cyclic olefin like cyclopentene which lacks cyclic structures in its backbone, this method of polymerization creates a polymer. So, it is known as ROMP. A cross-linked thermoset material results from the polymerization of vinyl.

3 Polymerization

Organic-inorganic materials are combined to form polymer nanocomposites, which have at least one filler phase with a dimension smaller than 100 nm [14]. Different synthesis methodologies are used to generate polymer nanocomposites. In Fig. 3 and Table 1, various synthesis techniques and polymers are mentioned.

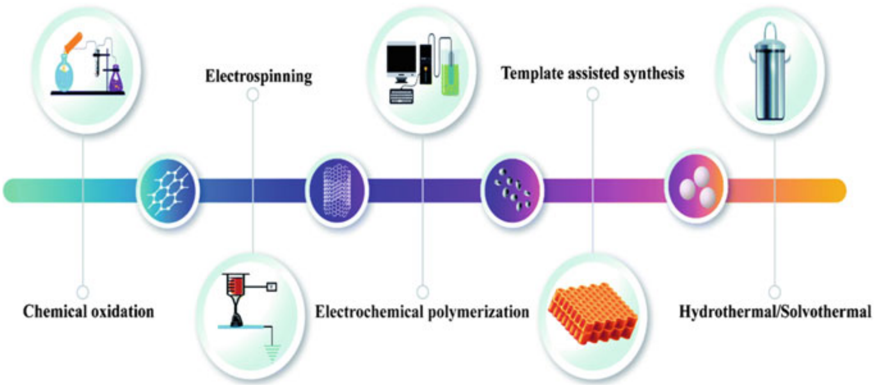

Fig. 3 Different synthesis methods for conducting polymers [101]. Copyright (2021) American Chemical Society

Table 1 Synthesis methods and polymer

Synthesis methods	Polymer/polymer composite	References
Melt intercalation	Thermoplastic polymer nanocomposites	[14]
Prepolymer intercalation	Poly(ethylene oxide), Poly(vinyl alcohol), Poly(acrylic acid), Poly(vinylpyrrolidone)	[14, 15]
In-situ polymerization	Thermoplastic- and thermoset-based nanocomposite, PPy/GO	[14]
Copolymerization	Coordination polymer	[16]
Templated polymerization	5′-acylamido-substituted DNA-template	[17]
Solid-phase synthesis	Pseudo-peptides	[17]
Liquid-phase synthesis		[17]
Suzuki cross-coupling		[18]
Yamamoto reaction,		[18]
Sonogashira-Hagihara reaction		[18]
Oxidative coupling reaction		[18]
Schiff-base reaction		[18]
Friedel–crafts reaction		[18]
Phenazine ring fusion reaction		[18]
Cyclotrimerization		[18]
Direct (hetero) arylation polymerization	2-iodo-3-octylthiophene	[19]
Ionic polymerization	Methacrylate of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl	[20]
Radical polymerization	Polystyrene, Polyethylene, Poly(vinyl chloride)	[21]
Polycondensation	Oxyacids and esters	[22]
The grignard reaction	Alkyl halides	[23]
Microwave polymerization		[24]
Chemical oxidative polymerization	Polypyrrole	[25]
Vat polymerization		[26]
Solution deposition polymerization	PMMA	[27]

4 Optical Sensor

Optical sensors are nothing more than detectors that track changes in a material's optical properties and turn them into an electronic signal, such as light [28]. Optical sensors emphasise the change in the transducers surface optical characteristics, which groups the target and the recognition component into a complex [29]. The two types of optical sensors are direct optical signal and indirect optical signal. In contrast to indirect optical sensors, which are based on binding event detection and signal amplification, direct optical sensors feature signal creation based on the growth of complex on the transducer surface. Optical sensors are classified into different types of sensors. Numerous materials are used to test optical sensing applications. We are studying polymeric material for optical sensing application. Optical chemical sensors works through optical transduction techniques to produce analyte information [30]. The most often used optical sensing technology is optical absorption and luminescence. Optical parameters like intensity, wavelength, permeability, phase, and luminescence are tracked by optical sensors after coming into contact with an analyte [31]. The most recent optical sensors are calorimetric, electrochemiluminescence, fluorescence, and surface plasmon resonance. Conducting polymer nanocomposites (CPNCs) sensing capabilities are influenced by the compounds, monomers, sizes, and microstructure. Electrical conductivity and a surface ability to interact with analytes and environmental factors are provided by the polymer chain. a polymer's ability to conduct electricity due to delocalized electrons in the chain's backbone [31]. In the unsaturated backbone, the delocalized electron creates channels for the charge carrier while moving freely. The catalytic and adsorptive interaction of analytes on sensing substrates is necessary for the CPNCs sensing behaviour. The sensing application is adjusted based on factors like microstructure and functioning. Following are some discussion points regarding polymeric materials optical sensing application parameters. The sensing system is discussed in more detail in the following paragraph.

The transmitted beam was gathered at the optical power metre using a set of lenses after it interacted with the sensing component while being exposed to dampness. It was observed that as the chamber's humidity increases, the output power increases linearly. The enhancement in output power proportional to the RH% can be explained by the chemisorption and physisorption of water molecules on the sensor element's porous surface. As was previously mentioned, there are three separate sensor response ranges such as 10–30% RH, 30–60% RH, and 60–90% RH. Throughout other ranges of %RH, the sensitivity is highest in the low humid range and as the %RH rises, the sensitivity falls. Water molecules quickly adhere to the films porous surface when it is exposed to humidity. Chemisorption occurs quickly in the low-humidity zone and substance M + (metal cation) establishes a potent chemical interaction with the water molecules OH anion. Due to the material's refractive index substantially decreased as a result of the humidity exposure, light is sharply bent. As a result the output power at the detector significantly increases. Ionic bonds are created with the substance during the chemisorption processes. This bond formation typically causes the material's refractive index to fall as a result of exposure to water because water has a lower refractive index than the material. Because of this reduction in refractive index, light often bends. Chemisorptions occur on the film's surface as well as in the pores as the humidity level rises. When exposed moisture first interacts with the active centres that have previously come into contact. Although the surface of the film and its pores both serve as active centres for chemisorbed water molecules, the pores larger aspect ratio makes them more effective. Figure 4 schematic illustration explains the sensing process.

This contact further causes light to bend, which results in an even greater rise in output power. Higher ranges of RH cause physisorption on capillary walls, which eventually leads to water vapour condensation. This film's capillaries become meniscus-filled with these condensed vapours, which results in a greater reduction in refractive index. At this point, the detector experiences its highest transmission power. Moreover the material is ionised by the humidification in the form of hydronium ions (H_3O^+), which lower the sensing elements refractive index by ionising the substance. Light bends as a result of this drop in refractive index. Thus, a consistent rise in output power is explored together with a corresponding rise in humidity [8]. Additionally, one more example of sensing such as by varying the concentrations of PEDOT and $FeCl_3$ as shown in Fig. 5, fabrication of PEDOT fibres with an oxidative catalyst ($FeCl_3$) resulted in fibres with conductivities that ranged from 0.02 to 0.28 S cm^{-1}. The technique might be used to direct and encourage dorsal root ganglion

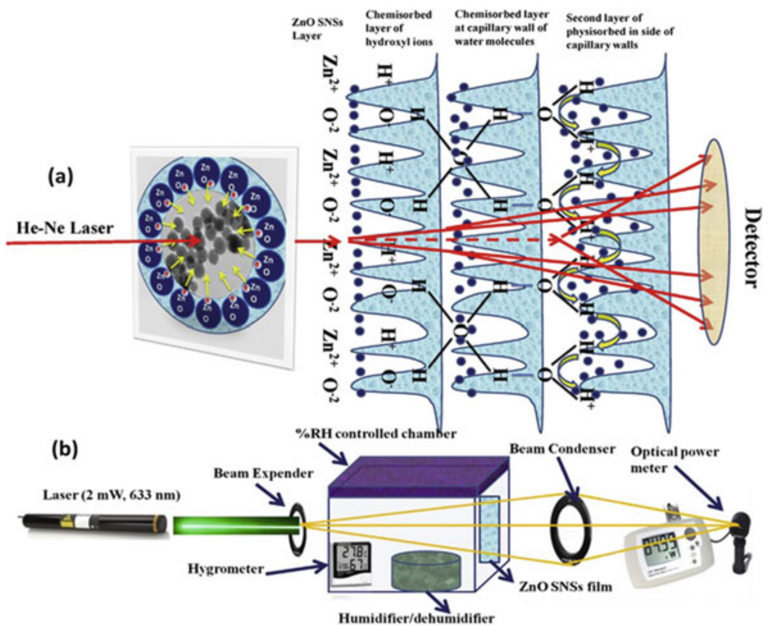

Fig. 4 **a** Ray schematic for the sensor mechanism. **b** Schematic for a transmission-based optical humidity sensing system [8]. Copyright (2018) Elsevier

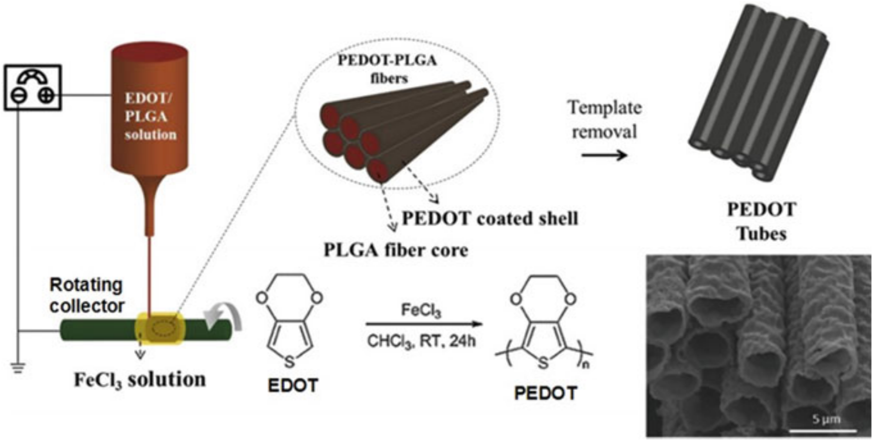

Fig. 5 PEDOT microtubes are synthesised utilising electrospun PLGA core/PEDOT shell microfibre templates that are aligned [27]. Copyright (2020) Elsevier

neuron growth, and the synthetic fibres could be utilised to carry drugs. Further, the basic terms of optical sensing are described.

According to IUPAC, sensitivity is “the capability of an analytical method to discriminate small differences in concentration of the test analyte.” The slope of a plot of the signal (signal response) against the analyte concentration is the simple definition of sensitivity. The change in any analytical signal (S) with the change in concentration (c) is therefore the definition of sensitivity. Unfortunately, a lot of authors conflate sensitivity with the limit of detection (the smallest amount of analyte that can be confidently detected, often at a signal-to-noise ratio of 3), but this is less common when it comes to pH sensors than in a lot of other cases, including biosensors [32]. Further, Response time is the period of time the sensor requires to complete 90% of the experiment during the adsorption of humidity whereas recovery time is the period of time required during the desorption [33].

Because optical fibre is used to transmit light in the majority of opto-electronic sensors this technology is appealing. For the transmission of light, optical fibre functions like a waveguide [34]. The benefits consist of:

- Optical fibres have a vast wide-band and low attenuation, making them ideal for long distances.
- Dielectric materials that are chemically inert are used to make optical fibres. Due to their resistance to electromagnetic interference, these sensors are reliable.
- These are lightweight systems due to their tiny size, simple geometries, and use of optical fibre.
- Optical fibre can be utilised to create biomedical instruments since it is biocompatible.
- Optical fibres can be employed at high temperatures, for example in blackbody-based sensors, because they have a high fusion point.

- Compared to typical electrical-based sensors, optical fibre sensors have substantially higher sensitivity, dynamic range, and resolution [35, 36].

Further, optical sensors compared with other types of sensors such as polymer-based gas sensing materials are often used to detect a variety of VOCs or solvent vapours in the gas phase such as alcohols, aromatic compounds, and halogenated compounds. Several studies examine the application of these materials in detecting inorganic gases including CO_2 and H_2O. The physical characteristics of the polymer layers such as their mass and dielectric properties will alter following gas absorption, much like metal oxide semiconductors when they are exposed to analyte vapour. High sensitivity and quick response times are two benefits of polymer-based gas sensors [37]. Other drawbacks of polymer-based gas sensors include long-term instability, irreversibility, and low selectivity. Whereas Almost all of the humidity sensors based on polymers operate at room temperature due to polymers high sensitivity to heat [38]. The first accounts of the development of luminous thermometers made using polymers originated in 2003. Fluorescent dyes that can be polarised and aggregatable polymers are additional ingredients in these mixes [5]. Additionally, there are known instances of temperature sensors based on optical microfibres that are integrated into polydimethylsiloxane (PDMS) as active interferometer elements. By removing impurities and delaying ageing, this polymer serves as a protective layer for the entire system. Fibres shaped into a cone with the right particular geometry were used to construct the interferometer. The instrument can measure temperatures between 20 and 48 °C, and it can detect temperature variations as small as 3101.8 pm/°C. Additionally, in order to create thin, dissociable polymer films, poly(2-hydroxyethyl methacrylate) and 2-dimethylaminoethyl methacrylate have been combined. These films which have a thickness of about 10 m, are highly sensitive and precise at determining the levels of hydronium ions in the immediate environment. Analysis was also done on the impact of varied polymer coating thicknesses on variations in potentiometric responses. Another material that has shown great promise for use in electronics is poly(p-phenylenediamine, or PPV). It is a conjugated polymer and the presence of both delocalized bonds on the aromatic rings and double bonds in the carbon chain allows us to assess how well it conducts heat. The usage of PPV in contemporary pH sensors is due to the fact that it also demonstrates photoconductive capabilities. A relatively recent class of intelligent materials are stress sensors. They are based on the phenomenon of photoluminescence. Colours produced by deformation depend on the types of forces applied to the material, such as stretching or shearing. The sensor that employed oligo(p-phenylene vinylene) as a dye is an intriguing example. It has a unique capacity to produce bright fluorescence in solution and a crystalline state as well as a range of chemical structures. Low density polyethylene (LDPE) was initially treated with this colour when it was still plastic. Stretching causes the material to glow, which gives it its distinctive properties. The injected dye clumps within the polymer matrix prior to deformation, resulting in excimer emissions. Then, under the action of stretching dye clumps are dissociated and the ionised form of this chemical exhibits luminescence with various properties. The polymer functions as a conductive element or a matrix of an electrically

Table 2 Polymer and their sensing applications

Polymer	Application	Properties	References
Polypyrrole	Glucose detection	Electro polymerization of pyrrole results in the electrode immobilisation of enzymes	[39]
Polyaniline	Triglyceride, urea, glucose sensor	Electrochemically controlled polymer deposition and enzymatic immobilisation	[40]
Polyamine	L-amino acid sensor	Electro polymerization for enzyme immobilisation	[41]
Poly(vinyl chloride)	Examination of urines creatine levels	Natural electrically inert lipids are applied as plasticizers to a polymer membrane	[5]
Poly(o-aminophenol)	Glucose biosensors	A plated glassy carbon electrode with an amperometric sensor	[42]
Redox polymers capable of crosslinking	Biosensors for enzymes	Use of polymers having cross-linking capabilities	[42]

conductive system in ion sensors. The measurement system interacts or exchanges ions with the analyte when such an arrangement is present. This occurrence is then interpreted as a registered electrical signal. Ion-selective electrodes (ISEs) are a few examples of these sensors. Despite the presence of other dissolved ions they enable the detection of certain ions in solutions. The various polymer and application are mentioned in Table 2.

4.1 Polymer

A unit structure repeats in organic polymers which are macromolecules [38]. Carbon-hydride compounds or their derivatives make up the majority of polymers. The backbone of the polymer is made up of a lengthy chain of carbon atoms that are connected to one another either by sigma bonds (single bonds) or sigma bonds + pi bonds (double bonds or triple bonds). There are two different kinds of polymers. Non-conducting polymers are placed after CPs. Conducting polymers such as polypyrrole (PPy) and polyaniline (PANI) [43] have longwave absorption that extends well into the near infrared (NIR) [28]. These exhibit outstanding optical, chemical, and electrical characteristics [44]. By using chemical or electrochemical techniques, conducting polymers can be generated. By copolymerization or structural derivatives conducting polymers molecular chain structure can be changed. Good mechanical properties of conducting polymers make it possible to make sensors quickly and easily. The conjugated macromolecules that make up the conducting polymers. When conducting polymers are protonated or deprotonated by specific chemical agents, their electrical and optical properties change.

The polymeric materials exhibited advantages such as.

1. An optical sensor has a recognition unit that may specifically engage with the target item that is sought as well as a transducer component that is used to signal the binding event [45].
2. Scientists are paying more attention to recognition components such as enzymes, antibodies, molecularly imprinted polymers, aptamers, and host–guest recognizers in order to enhance sensor analytical performance [45].
3. Based on FL, UV, Raman, SPR, or chemiluminescence signal fluctuations optical sensors offer a simple, quick, and affordable method for sensitive pesticide detection [45].
4. The use of thermo-responsive polymers to determine the intracellular temperature [46].
5. Polymer fibre tweezers are used to trap and identify single cells in a very intriguing and new biomedical application.
6. When compared to silica fibres, polymer optical fibres have appealing properties such as low Young's modulus, high failure strain levels, great flexibility, and biocompatibility. These benefits fit the instrumentation needs for tracking bodily processes and physiological changes in people [47].
7. Polymers are materials with a low cost. Simple fabrication methods for polymers (no requirement for specialised high temperature or clean room operations) [48].
8. The wide range of molecular structures available in polymers, along with the ability to incorporate side chains, charged or neutral particles and even grains with specific behaviours into the bulk of the material or on its surface, allow for the production of films with a variety of physical and chemical properties including also sensing behaviour [48].
9. Inorganic solid-state devices employ active sensing polymers as an essential component in the form of sheets or films. The latter are made utilising thin and thick film technologies processing of ceramics and glasses or monolithic semiconductor manufacturing [48].
10. Compactness, light weight, multiplexing capabilities, and immunity to electromagnetic fields are some advantages that polymer optical fibre (POF) curvature sensors have over traditional technologies for angle evaluation [49].

Optical-sensing techniques have gained a lot of attention recently and are frequently used for quantitative measurements of various analytes in environmental, industrial, clinical, medical, and biological applications including H^+, carbon dioxide, oxygen, metal ions, ammonia, amine, urea, glucose, humidity, and penicillin. Optical sensors have several benefits over other types of sensors. The signal is typically insensitive to sample flow rate, stirring speed, and external electrical interferences, does not require a reference, and does not typically consume analytes. Additionally, when optical fibres are utilised, optical sensors have the potential for miniaturisation, remote sensing, and simple installation [50].

4.1.1 Conducting Polymers

Conducting polymers get placed as essential polymer materials apart from the synthetic polymers [51]. After being doped with the right dopants, conducting polymers have a conjugated double-bonded backbone that demonstrates electronic conductivity. The conducting polymers are a component of polyenes or polyaromatics, including poly(p-phenylene), poly(acetylene), poly(aniline), polypyrrole, polythiophene, poly(pyrroloyl) (phenylene vinylene) [52]. These conducting polymers are used as optical sensor material. Optical sensor application of conducting polymers are discussed as given below.

Polypyrrole (PPy)

PPy is a conducting polymer which possess excellent optical sensing properties. Marcos et al. [53] investigated optical sensing properties of PPy films at various pH. The PPy spectra displayed high near-infrared absorption at about 900 nm and minimal absorption at about 550 nm. pH values between 6 and 12 affect the spectrum's shape and intensity. Marcos et al. [54] reported characterisation of PPy films for optical sensing application. By using several oxidising chemicals, including aqueous ferric chloride, author synthesised PPy thin films using chemical oxidative polymerization. After a 20–30 min reaction period, homogenous thin films were produced and placed on plastic supports like polyester membranes and polystyrene slides. Long-wavelength absorption band that spans far into the near infrared is what distinguishes the PPy thin films from other materials absorption spectra (NIR). With exposure to ammonia vapours and a change in pH, the PPy NIR spectra shift.

Polyaniline (PANI)

PANI is an intrinsic conducting polymer by nature [33]. Electrical conductivity of PANI ranges from 10^{-13} to 10 Ω^{-1} cm^{-1}. PANI can be synthesised chemically by utilising a variety of polymerization agents, including hydrogen peroxide (HNO_3), ammonium persulfate, copper sulphate, hydrogen peroxide, and potassium permanganate [55]. Hard template, soft template, electrochemical polymerization, photochemical polymerization, mechano-chemical polymerization and enzymatic polymerization are the synthesis methods of PANI. When PANI films were subjected to low aqueous ammonia concentrations, their optical response was examined. In the process of manufacturing the PANI films, chemical bath deposition was used. To determine the optical sensitivities when the PANI films were exposed to different concentrations of aqueous ammonia (10–4000 ppm), the optical transmittance of the PANI films was measured in the wavelength range of 350-1100 nm [44]. Jin et al. [56] reported the construction of an optical ammonia sensor based on PANI. In a room temperature chemical oxidation process, the author prepared PANI films using aniline monomer. The optical ammonia gas sensor in this instance responds in less than 15 s and regenerates quickly, taking less than 2 min at ambient temperature. The sensor has a linear dynamic range of 180 to 18000 ppm and an ammonia detection limit of 1 ppm (v/v). PANI films were synthesised by Ahad et al. [35] using three distinct temperatures for polymerization (−5, 0, and 25 °C). With a sensitivity value of 0.0015 and a reaction time of 7s, the PANI displayed the highest conductivity at 0 °C, which is 1.627×10^{-2} S/cm. The performance of the sensor was examined using the characteristics of recyclability, selectivity, limit of detection, and limit of quantization. PANI is utilised in this instance to detect chloroform and is coated with Fiber Bragg Grating (FBR). The PANI coated Fiber Bragg Grating (FBG) sensor demonstrated excellent recycling up to 10 cycles in the detection of chloroform. The optical sensor lower limit of detection (LOD) was 9.22 ppm and its limit of detection (LOQ) was 27.9.

Polythiophene (PTh)

Conjugated PThs and their desired derivatives are introduced as new members of the conjugated polymer group due to their particular properties, such as electrical behaviour, thermal stability, high environmental behaviour, mechanical robustness, and cost-effective manufacture [57]. The regioregularity, backbone conformations, and aggregation states of water-soluble PThs in liquids or solid states all influence their optical characteristics [58]. The chemical and electrical architectures of conjugated backbones have a dominant influence on the photophysical characteristics of PThs. As a result PThs with different side groups and identical backbone architectures exhibited similar optical characteristics. Wadatkar et al. [59] investigated optical study of chemically synthesised conducting polythiophene with the help of UV-Vis Spectroscopy. Here, author prepared conducting polythiophene (PTh) using an anhydrous ferric chloride ($FeCl_3$) oxidant at various concentrations and thiophene as the monomer at ambient temperature. The UV-vis spectroscopy is used to investigate optical characteristics. From absorption spectrum ranges of 200–500 nm, the optical characteristics of PThs samples are calculated. The PThs have absorption between 200 and 250 nm. PThs have an optical band gap energy that varies from 4.033 to 4.688 eV.

4.1.2 Non-conducting Polymers

The non-conducting polymer layer possess immobilisation substrate with transducing elements which are useful for the fabrication of electrochemical biosensors [60]. Poly(vinyl alcohol), polystyrene, poly(methyl methacrylate), and poly(vinyl acetate) are the well-known nonconducting polymers [61]. These non-conducting polymers act as optical sensors as given below.

Polyvinyl Alcohol (PVA)

Simple alkenyl monomers with carbon-carbon double bonds, also known as vinyl polymers serve as the building blocks for polymers [62]. Wong et al. [42] looked into the optical sensing capabilities of a polyvinyl alcohol fibre covered with a photonic crystal for measuring humidity. The author made PCF covered PVA by collapsing the holes at both ends in order to make a Michelson interferometer with cladding type excitation. Low hysteresis, great repeatability, low cross-sensitivity to temperature and ammonia gas and stability were all exhibited by the sensor. It had 0.60 nm/% RH high sensitivity and was coated with 9% (w/w). Gaston et al. [63] looked into temperature, relative humidity, and pH sensor designs that use optical fiber-based sensors. From 70 to 90% relative humidity, PVA films on the fibres exhibited 10 dB linear variation.

Polyoctopamine (POct)

POct is a non-conducting polymer with amine functionalization. In an electrochemical biosensor, it serves as the transducer layer [39]. Polymers have flexible covalent coupling by carboxy, aldehyde, or thiol liner conjugation without any surface activation.

Polystyrene (PS)

A few of the desirable properties of polystyrene are its high melting point (270 °C), low specific gravity (1.045), excellent hydrocarbon resistance, high degree of dimensional stability, superior mechanical performance at high temperatures, and very good electrical properties (PS) [62]. Burratti et al. [64] investigated the photonic crystals optical sensing capabilities using self-assembled polystyrene nanobeads Many alcohols can be detected using a PC, including n-butanol, ethanol, 1-propanol, isopropanol, and methanol by modifying the reflectance spectrum driven on by the vapour condensation inside the pores of the PC as shown in Fig. 6. The observable wavelength redshift of the reflectance peak is due to the systems higher refractive index and the enlargement of PS spheres generated by the alcohols. The PCs exhibited complete reversibility. PS photonic crystals can detect the ethyl alcohol content of various water/ethanol mixtures.

Panawong et al. [65] investigated the enhancement of optical sensing properties through the polystyrene introduction and porous structure. The author described a quick and effective process for creating an optical sensor for the detection of Fe^{3+} based on fluorescence quenching. The PVS-g-PS membrane demonstrated excellent reusability and highly sensitive and selective responses to Fe^{3+} over other chosen metal ions. Lutti et al. [66] proposed a monolithic optical sensor based on polystyrene microsphere whispering-gallery modes. The author here showed an optical sensor system based on the detection of strong whispering-gallery modes in PMs coupled to

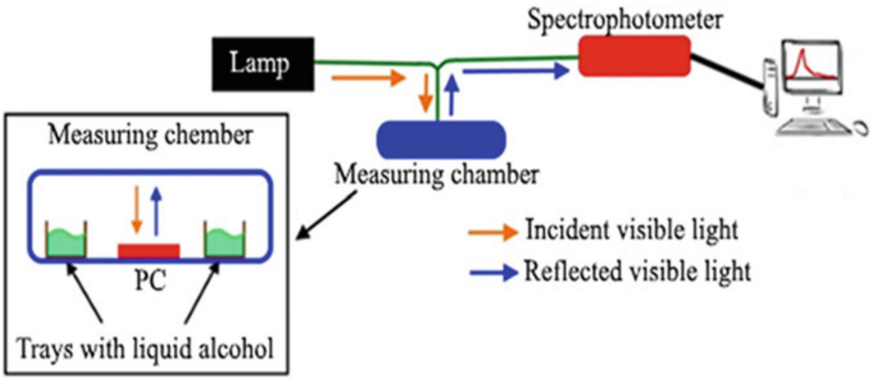

Fig. 6 Experimental setup for normal incidence reflectance measurements [64]. Copyright (2018) Elsevier

a glass coupler using a solid separation layer index suitable for water. A monolithic device development that can achieve controlled spacing between the optical coupler and the micro resonator without using piezoelectric positioning tools. Giordano et al. [67] examined the optical sensing capabilities of ultrathin films made of syndiotactic polystyrene in the δ-form for the detection of chloroform. Here, the author looked at how exposure to $CHCl_3$, which is utilised as a transduction property, changed the polymers refractive index as a result of chloroform sorption into the polymer layer. a fibre optic refractometer for measuring reflectance that coats a nanometric sPS layer with chloroform at very low pressure producing high sensitivity, rapid reaction times, and excellent reversibility. Scarmagnani et al. [68] used spiropyran photoswitches to study the optical sensing capabilities of a polystyrene bead-based system. The author described the various immobilisation techniques used to immobilise spiropyran derivatives on the surface of polystyrene microbeads. Using low power light sources like light-emitting diodes, the functionalized polymeric beads can be reversibly altered between the colourless, inactive spiropyran (SP) and the vividly coloured (purple), active merocyanine (MC) forms (LEDs).

Poly (Methyl Methacrylate) (PMMA)

PMMA is a synthetic polymer which is prepared from the methyl methacrylate monomer [69]. PMMA is obtained from its monomer with the use of different methods of polymerization. PMMA improved the behaviour at the carbon nanotube and copolymer contact. The best material for chemical sensors is a composite made of carbon nanotubes (CNT) and PMMA or modified CNT. Zhang et al. [70] investigated optical sensing properties of PMMA for humidity responsivity. The author used optical fibre Bragg gratings to examine the PMMA's sensitivity to dampness (POFBGs). The characteristic wavelength of the grating is affected by both the fiber's altered refractive index and swelling brought on by water absorption. Devikala et al.

[71] investigated gas sensing properties of ammonium dihydrogen phosphate-PMMA composite. Using optical techniques, the author studied the PMMA's sensitivity to humidity. The sensitivity of the gas detector is expressed by a change in the composite film's resistance, according to the author, when gases are exposed to it. Over time, the polymer composite's electric resistance rose in the presence of acetone vapours and came to equilibrium. Miluski et al. [72] investigated optical sensing properties of xanthene dyes doped PMMA microspheres. According to the author, polymeric structures showed significant levels of doping and good processability. The xanthene dyes, which were utilised as luminous markers, included Fluorescein (F1) and Rhodamine B (RhB). The suspension polymerization of PMMA microspheres was used to carry out the doping process for these colours. At 510 and 595 nm wavelengths, the luminescence was extremely bright. Optical measurements were made to determine the sharpness and size distributions of manufactured microspheres.

Polyvinyl Acetate (PVAc)

The reactivity of acetylene monomers depends on the triple bond electronic density and the π-bond energy. [73]. The π-bond energy of acetylene is 54 kcal/mole, whereas that of ethylene is 65 kcal/mole. Khamidy et al. [74] investigated the efficiency of polyvinyl acetate nanofibres doped with citric acid for ammonia sensing is influenced by the dopant concentration. The author tested the PVAc's sensing capabilities using inexpensive routes. Author experimented with different ammonia vapour concentrations applied to CA-doped PVAc nanofiber to study sensing performance factors such as limit of quantification (LOQ), repeatability, limit of detection (LOD), and sensitivity. The LOD and sensitivity values are 1 ppm and 1.34 Hz ppm^{-1}, respectively. High CA dopant concentrations linearly increase sensor sensitivity while also extending response and recovery durations. Mahmoud et al. [75] studied the PVAc/bismuth oxide nanorods optical characteristics. The nanocomposite of PVAc and bismuth oxide (Bi_2O_3) was prepared. The nanocomposite displayed spectrum absorption between 300 and 800 nm. Here, the $\pi-\pi^*$ interband electronic transition is what causes the absorption peak at 320 nm. As the concentration of bismuth oxide rises, the absorption peak shifts towards the longer wavelength area.

4.2 Polymeric Materials

PPy is a well-known conducting polymer. It is widely used in optical sensing applications. In optical sensing, PPys composite [76] also plays a crucial role. The backbone of the polymer, which is a lengthy chain, is polymer. The backbone is coupled with functional groups, which may be either single atoms (such as oxygen or halogen) or molecular groups (e.g., –COOH, $–NO_2$) [38]. Ferreira et al. [77] investigated optical pH sensitivity of bromophenol blue-doped polypyrrole material. By using electrochemical synthesis, the author produced polypyrrole doped with bromophenol blue.

The pH range for the material is 1.5–11.0. The substance was accurate, recurrent, and reversible. When exposed to 11.0 pH, PPy-BPB films undergo permanent spectrum alterations due to irreversible reduction. Goncalves et al. [78] examined cellulose paper/polypyrrole/bromophenol blue (CP/PPy/BPB) composite optical characteristics. The CP/PPy/BPB composite was made by the author via in situ polymerizing pyrrole on a CP matrix that had formerly been BPB treatment. The CP/PPy/BPB exhibit a pH-dependent response with various colours as well as sensitive to pH alterations and ammonia concentration variations. CP/PPy/BPB is a leading candidate for acid-base and ion selective sensing.

PANI composites are appropriate for effective sensing of basic substances [79–81]. PANIs are useful for detecting acidic compounds in their undoped state. In optical sensor devices, composite film prepared of PANI and poly(ethylene terephthalate) (PANI/PET) works efficiently. PANI is deposited on PET film. The ratio of PANI doping affected both the composite optical density and surface resistance. Gicevicius et al [82] investigated the composite of o-phenylenediamine and PANI's optical characteristics. The author prepared a composite by copolymerizing PANI and o-phenylenediamine. Potential cycling was used to potentiodynamically develop glass electrodes coated with ITO and covered with PANI and poly(aniline-co-o-phenylenediamine) (PANI-co-oPD) layers. Here, spectrophotometric titration was used to estimate the features of optical pH sensing. By altering the oPD molar fraction of the polymerization solution from 0.25 to 2%, the pH in this experiment was changed from 5.8 to 6.7. Optical pH detecting characteristics changed with pH level.

Several materials can be combined with thiophene [36]. Most conjugated nanoparticles are combined with polymers. Composites provide stability and aid in achieving desired performance. According to Goncalves et al. [60], one benefit of optical sensors is that they are appropriate for remote detection. Optical sensing offers a lot of flexibility at a reasonable price. The detection of six volatile organic compounds and water vapour in the 500–30,000 ppm concentration range was accomplished using optical sensors and thin films of seven polythiophene derivatives as the active layer. Evans et al. [61] synthesised a composite of a conjugated polyelectrolyte called poly[3-(6-trimethylammoniumhexyl) thiophene] (P3TMAHT). In the presence of anionic surfactants, it was found that the cationic conjugated P3TMAHT's absorbance and photoluminescence spectra changed significantly as a result of ionic complex formation and self-assembly. Several colorimetric transitions result from the addition of an anionic surfactant to a P3TMAHT solution in D2O. Because anionic surfactants can select discriminating different structural subgroups by dual mode detection, the P3TMAHT is an efficient optical sensor.

An optical sensor investigation was based on carbon quantum dots (CQDs) wrapped in molecularly imprinted polymers (MIPs) by Ensafi et al. [62]. This was designed to enable the sensitive and precise measurement of promethazine hydrochloride (PrHy). Orange juice was used as the carbon source in a straightforward, inexpensive, and environmentally friendly method to create water-soluble, fluorescent CQDs. The CQDs' principal benefit was their low toxicity. Sol–gel polymerization was used to cover the CQDs surface in MIPs matrix. At PrHy concentrations between 2.0 and 250 μmol L^{-1}, with a detection limit of 0.5 μmol L^{-1}, the

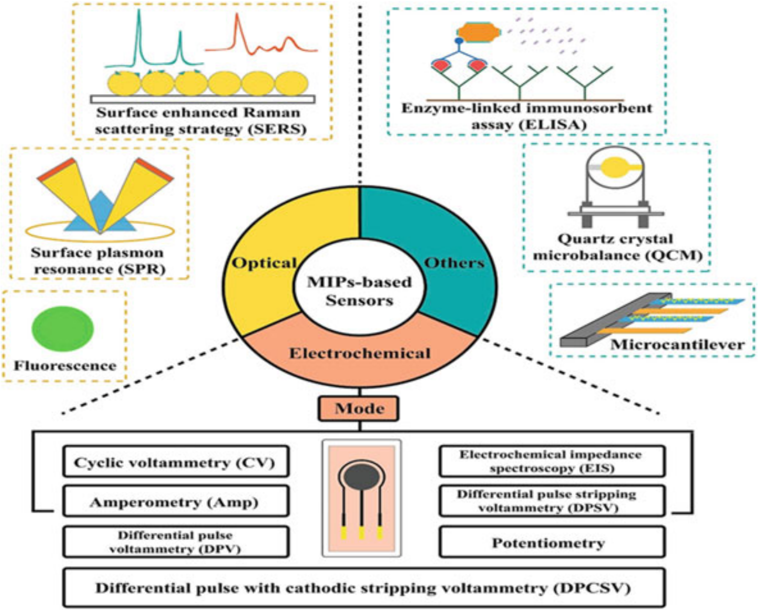

Fig. 7 The various types of MIP-based sensors [102]. Copyright (2019) Elsevier

CQDs-MIPs fluorescence intensity responds linearly, 20 μmol L^{-1} of PrHy was used to test the reproducibility value and the result was 5.1 RSD%. MIP-based sensors can be seen in Fig. 7.

Applications for MIP-based sensors include pH and humidity sensors. The great sensitivity, straightforward design, and effective refractive index sensing of microfibre resonators have recently drawn a lot of interest. The microfibre loop resonator (MLR) is a straightforward device to build because of the electrostatic forces or van der Waals that maintain the loop structure at the joint area. Irawati et al. [83] suggest and demonstrate that relative humidity monitoring is possible using a PMMA microfibre loop resonator (PMLR) wrapped in a zinc oxide (ZnO) nanostructure. A PMMA microfibre with a 6 m diameter was used to build the PMLR, which has a loop diameter of 56 m. The findings demonstrated that the extra ZnO nanostructure coating on the PMMA fibre surface increased the sensor's sensitivity. When the sensor was precisely positioned inside a hermetically sealed chamber, less transmission was experienced. This observation served as the basis for the device operating mechanism. The output power of the PMLR with ZnO nanostructure coating declines linearly from −9.57 to −20.19 dBm when the relative humidity level varies from 20 to 80%, with a maximum sensitivity, linearity, and resolution of 0.1746 dBm/%, 94%, and 6.17%, respectively. The great sensitivity of traditional silica fibres is combined in this work with the toughness and flexibility of PMMA fibres, making them ideal for continuous relative humidity monitoring in small spaces.

In the presence of H_2, Kadir et al. examine the abilities of a nanoporous Nb_2O_5 layer to sense light. By anodizing Nb metal sheets produced by RF sputtering onto FTO glass substrates, nanoporous Nb_2O_5 films were generated [84]. The Nb_2O_5 films were formed using the same electrolyte. Experiments were performed with the help of optical gas test chamber (as shown in Fig. 8) to identify the morphological and crystalline properties of Nb_2O_5 films as well as the optical changes that arise from interactions with hydrogen gas molecules on these films. For comparison, the interactions of the films to the gas molecules, ethanol and methane were also studied. Under various operating temperatures, the nanoporous Pt/Nb_2O_5 films optical response towards hydrogen gas was initially studied. In order to conduct the measurements, it was alternatively exposed to 1% hydrogen gas and synthetic air at temperatures of 22, 40, 60, 80, and 100 °C. The test chamber was not used at temperatures above 100 °C since it could not withstand them.

At room temperature, it was discovered that the Pt/Nb_2O_5 film did not exhibit any visible gas reaction, as shown in Fig. 9a. It is considered that the absence of energy at such a low temperature prevents the hydrogen gas molecules from separating. When Pt/Nb_2O_5 films were exposed to 1% hydrogen gas at 100 °C, from 350 to 900 nm, across a broad wavelength range, the absorption spectra varied (Fig. 9b).

The adsorption rate of H^+ ions increases at the high temperature of 100 °C because there is sufficient energy present to breakdown molecular hydrogen, and at the same time, the effective surface area available for the gas adsorption reaction is increased since the surface capacity to produce water vapour is limited. In this way, various material [85] and their composite [86–88] optical properties are studied in this chapter.

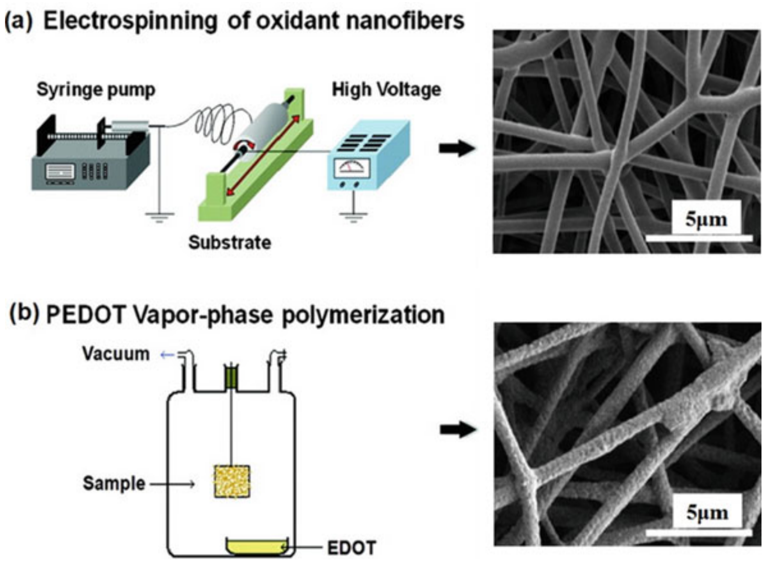

Fig. 8 The two-step synthesis of PEDOT nanofiber. Copyright (2020) Elsevier [27]

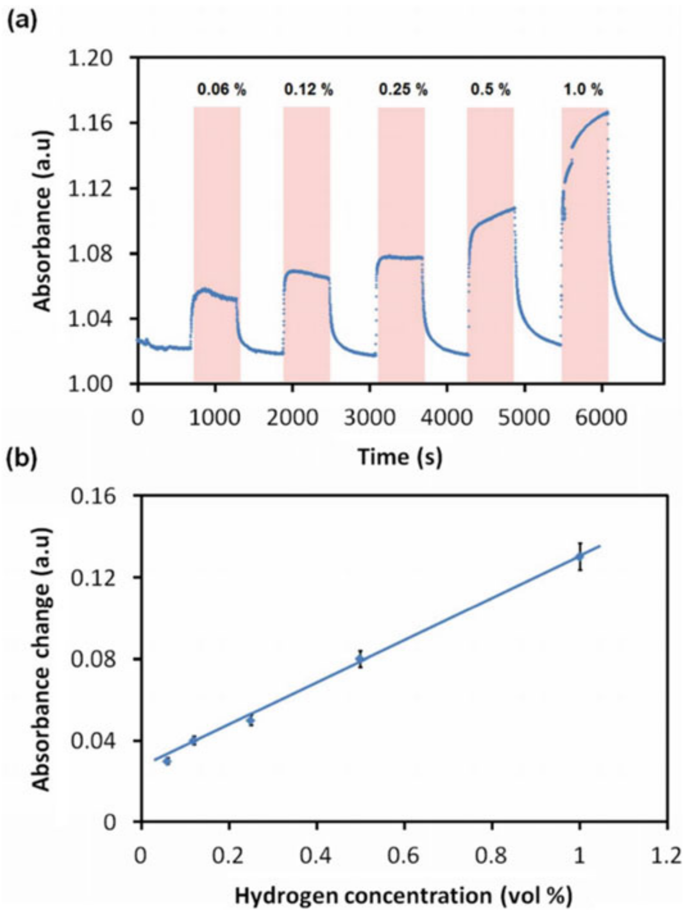

Fig. 9 **a** Dynamic performance and **b** absorbance change of nanoporous anodic Pt/Nb_2O_5 films after exposure to different concentrations of hydrogen gas at 100 °C at the wavelength of 600 nm. Copyright (2015) ACS [84]

4.3 Biopolymer

Biopolymers are frequently derived from natural or live sources. They stand in for a particular class of polymeric compounds. Such substances abound and can be categorised as polynucleotides, proteins, polysaccharides, and others having multiple monomers [89]. Biopolymeric structures come in a variety of sizes and forms. Uneven particles, scaffolds, rods, and fibres are a few examples of what is available. Their morphology defines their characteristics and potential application areas. Biopolymeric spherical particles are particularly intriguing since their form makes injection easier and they are appropriate for applications in medicine. The biopolymers may be produced chemically from natural starting materials (such as starch, sugar, maize, etc.) or by biological systems (microorganisms, plants, and animals). The following are examples of biodegradable biobased polymers: (1) synthetic polymers made from renewable resources, like poly(lactic acid); (2) biopolymers made by microorganisms, like PHAs; (3) naturally occurring biopolymers, such as proteins and starch; or by definition, natural polymers are those produced through biosynthesis in the biosphere [90]. Nucleic acids, which make up DNA and RNA, polypeptides or proteins, which are composed of amino acids that are coded by nucleic acids, and polysaccharides, which are intricate molecules built of carbohydrates are a few examples of common biopolymers [91]. Since biopolymers are readily available low/nontoxic, biodegradable, biocompatible, chemically adaptable, and intrinsically useful, they are highly potential for a wide range of applications including biomedicine, food, textile, and cosmetic [92]. Construction, aerospace, food, and biological disciplines are just a few of the areas where 3DP technology has great potential.

The ability of biopolymers to gather and accumulate analytes on sensor surfaces, their suitability for use on objects like thin adherent films (sensing skins), and their chemical structure-dependent selective interactions with the vapour make them useful materials for chemical vapour analysis [90, 93]. Making sensors with quick, reversible, and repeatable feedback is possible with polymers. Additionally, different combinations of polymer nanocomposites can be used as sensor arrays, adding variable selectivity that is adequate to obtain valuable chemical information for pattern-recognition analysis. Scientific research on the chemical structure, physicochemical properties, and applications of biopolymers has increased as a result of their excellent biological characteristics, which include an abundant and renewable supply, low cost, biodegradability, antimicrobial activity, biocompatibility, renewability, and adsorption properties [94]. Natural biopolymers are good options to build high performance conductive hydrogels due to their structural traits as well as their inherent biological properties. Al and heavy metals are both commonly present in the environment. While traditional analytical tools like atomic absorption spectrometers and inductively coupled plasma mass spectrometers were previously used extensively for the detection of certain metals, biosensors are now being touted as potential substitutes. A biosensor is an analytical tool that joins a biological element and an electronic gadget so that the biological element's response can be recorded and converted into a readable electronic signal. For the detection of heavy metals and Al, a number of sensitive enzyme-based biosensors have been created to date. These include the urease conductometry biosensor, α-chymotrypsin amperometric biosensor, acetylcholinesterase optical biosensor, and invertase-mutarotase-glucose oxidase-based conductometry biosensor [95]. A common and applicable method for food preservation is food packaging. The use of natural, biodegradable, and bioavailable polymers in food packaging is growing [96]. Further, the biopolymer and conducting polymer-based materials were used in optical sensors for the detection of heavy metal ions [3]. The day when biobased polymers replace conventional polymers is getting closer than ever to that point. Nowadays, biopolymers are widely used in a wide range of applications, from low-tech to high-tech, as a result of improvements in bioprocessing technology and growing consumer interest [90]. The traditional petroleum-based composites are starting to be replaced by the development of biocomposites employing biopolymers. Additionally, the development of chemical sensors employing biopolymers may make it easier to detect chemicals. In such a way, biopolymers play a vital role in optical sensing.

Personalised wearable smart gadgets have experienced significant growth thanks to the development of the 5G platform and artificial intelligence. In the meantime, new ideas, new technologies, and new goods made of useful materials are still being researched globally. The advanced technology of three-dimensional (3D) printing, sometimes referred to as additive manufacturing (AM), is based on a computer-aided design (CAD) model. The innovative use of 3D printing and functional polymers results in functionalized 3D printed polymer devices that are essential to the coming industrial revolution. The functionalized 3D printed polymer devices play a crucial part in the upcoming industrial revolution thanks to the clever coupling of 3D printing with functional polymers. As a young technology, 3D printing is always improving, with improvements to printing speeds and resolution. This novel manufacturing process must be suitable for large-scale production in order to genuinely enhance its advantage embedded in the AM nature compared to the standard subtractive measures and make 3D printing of functional products pragmatic towards solving real challenges in life. The equipment must meet severe time requirements since the robotic arms powered by electric motors need to move quickly and precisely. Further research should be done on parallel and independent three-axis robotic arms that permit simultaneous operations. The majority of the present 3D printing research has primarily focussed on processing a single material, which is not a practical real-world solution. The future of 3D printing should involve a one-stop shop, offering finished goods with integrated features that don't require post-assembly during a single scheduled printing cycle. This calls for a multiprocessing approach where different materials and even functional components must enter a process that is already in motion to start in situ assembly and integration. For the bulk manufacture of identical parts, traditional manufacturing processes like casting, forging, and machining are particularly well suited. For this reason, a highly compelling idea to replace conventional methods would be to realise rapid and large-scale production in a one-stop multiprocessing manner that generates multifunctional devices in customised and designated geometrical form factors. A cutting-edge industry that emerged during the information age is the 3D printing of useful objects. This digital manufacturing technology has a wide range of possible applications and a strong potential to transform traditional processing sectors thanks to the developing field of informatics. Imagine fabricating intricate sensors and interconnected devices using 3D printing in a distant satellite to replace ones that were inadvertently defective [97]. This would drastically cut the delivery time and shipping costs while also resolving critical issues. The only thing limiting the potential of the developing technology may be our own imagination.

Optical sensing is used in civil applications such as if (i) a conventional sensor fails to meet performance requirements (such as stability, accuracy, durability, etc.)

under specific conditions, or (ii) an optical sensor can provide useful information that is not possible with conventional sensors, optical fibre sensing systems may be used to replace current electrical systems. In many situations, it is also possible to combine conventional sensors and fibre optic sensors to have the best of both worlds (for example, vibrating-wire piezometers and fibre optic distributed leakage detection systems in the same dam). At the processing stage, data from the two systems can be integrated [98]. The concepts and benefits of such sensors must be thoroughly understood in order to pinpoint appropriate applications for the OFS. However, civil engineers frequently lack such comprehension. Additionally, MIPs are a cutting-edge technique for sensing molecules in the absence of a bioreceptor. The main challenges presently for MIPs are to locate an appropriate market for applications, develop standards, improve robustness, and scale up production. MIPs have moved beyond a simple proof of concept. It is a long and difficult process, but it is clear that MIPs have reached maturity, and serious efforts will be made to realise their enormous potential benefits in the form of inexpensive and reliable analytical devices that will lead to improvements in quality of life as well as daily applications in diagnostics and medicine [28]. To sum up, current advancements in MIP research could result in the development of a novel family of analytical sensing tools with broad and revolutionary applications in diagnostics.

4.4 Limitations and Challenges of Optical Sensor

Wearable strain sensors have recently exhibited remarkable sensing performance for future applications in human motion detection and soft robotics, thanks to recent developments in materials science and functional microstructures/nanomaterials. The design, integration, and safety of stretchy and wearable strain sensors still face several difficulties. Here, we discuss some of the key issues that must be resolved for the design of high-performance wearable strain sensors. First, it is currently difficult to construct stretchy strain sensors that can measure decoupled strains in several directions and multiplane deformations. To get over this restriction, more research should focus on innovative sensor architecture, 3D structures, and metamaterials [99]. The limitations of optical sensors are as follows.

1. susceptible to disruption by external factors
2. can be costly
3. Possibility of physical harm
4. It is still difficult to create stretchy strain sensors that can detect dissociated strains in several directions and multiple planes of deformation.
5. To maximise surface interaction sites between chemisorbed oxygen species and gas analytes, SMO NFs must be controlled for their distinct structure and appearance. High performance chemical sensors may ultimately result from multi-dimensional heterostructures like 1D-1D with various material compositions.

6. Only a small number of periodic table-found catalytic nanoparticles are currently being studied. Numerous distinctive catalysts with diverse components have been found for enhanced catalytic activities in the field of oxygen reduction electrocatalysts. To overcome the current constraint, a new class of innovative catalysts can significantly improve sensitivity and selectivity. To overcome the current constraint, a new class of innovative catalysts can significantly improve sensitivity and selectivity.
7. Requires heavy UV lights or spectrophotometers for fluorescence
8. Needs specially made probes
9. Development of unique algorithms is required for smartphone-based methods
10. Colorimetric and fluorescence sensors' dye biocompatibility
11. Massive size

The development of suitable and pleasant materials, fabrication techniques, and accuracy are among the issues facing wearable optical sensors. It is necessary to investigate more flexible materials, such as semiconductors and dielectrics. It is necessary to use multi-modality sensing, which entails using a single structure to detect various inputs and fix several sensors on a single platform. Due to the decreased reliability of non-invasive biofluids and the fact that hormone sensing requires preconcentration procedures and dilution of the analytes, hormone sensing should be prioritised in the case of wearable sensors. Light sources are needed for fiber-optic-based sensor designs like Bragg grating, Mach-Zehnder, and Fabry-Perot interferometers, and the sensor is large and expensive because of high-frequency physiological signals and modulation devices [100]. Aerospace companies use wearable sensors in a variety of products, including eye-tracking glasses, radio headphones, oxygen masks, helmets, cardiac monitoring devices, in-flight monitoring, and air quality management [103].

5 Conclusion

In this chapter, we discussed polymer synthesis methods that are types of polymerization. Here, we briefly discuss about what is optical sensing. Then we have highlighted the polymer types and optical sensing properties. The conducting polymer consists of Polyaniline (PANI), Polypyrrole (PPy), Polythiophene (PTh), etc. and non-conducting polymer consists of Poly (methyl methacrylate) (PMMA), Poly (vinyl alcohol) (PVA), Polystyrene (PS), Polyoctopamine (POct), and Poly (vinyacetate) (PVAc). We have discussed optical sensing properties of conducting polymers and non-conducting polymers in detail. Also, we discussed optical sensing properties of polymeric materials. These optical sensing properties are applicable to temperature sensor, pH sensor, humidity sensor etc. In this way, optical sensing is versatile in research areas.

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Utilization of Metallopolymer Nanomaterials in Optoelectronic Sensing

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Abstract Optoelectronic sensing technology has become increasingly important across a wide range of industrial sectors, and the use of metallopolymer nanomaterials (NMs) in this field has attracted significant interest due to their unique features. This chapter presents a comprehensive outline of the potential of metallopolymer NMs in optoelectronic sensing applications, covering topics such as basic operating principles, synthesis, sensing mechanism, and potential applications in areas like healthcare, environmental monitoring, and food safety. Metallopolymers offer advanced energy harvesting and sensing devices with excellent properties such as biocompatibility, low fabrication cost, and efficiency. The synthesis of metallopolymers has received significant research interest because of their numerous uses in areas like sensors, energy devices, and medical applications. The great potential of optoelectronic sensors to take humans' lives towards a comfort zone is grabbing researchers' attention. The chapter gives a summary of the recent advancements made in metallopolymer NM-based sensors and examines their performance in detecting various analytes such as gases, biomolecules, and heavy metals. It also highlights the

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current challenges and limitations of metallopolymer NMs in optoelectronic sensing and proposes potential solutions to address these issues. The concluding remarks emphasize the importance of continued research in this exciting and rapidly evolving field and suggest future directions for research that could lead to improved performance, reproducibility, selectivity, and stability of metallopolymer NMs in optoelectronic sensing applications. Overall, this chapter provides a valuable resource for researchers and practitioners interested in the potential of metallopolymer NMs in the field of optoelectronic sensing.

Keywords Nanomaterials · Optoelectronics · Devices · Metallopolymer · Sensors · Nanoparticles · Energy devices

1 Introduction

Technology of optoelectronic sensing has attracted considerable interest in the past decade, owing to its wide-ranging applications in different fields, such as healthcare, environmental monitoring, and food safety. Optoelectronic sensors are devices that can convert light signals into electrical signals, enabling them to detect and analyze various physical and chemical parameters. These sensors possess several benefits, including but not limited to high sensitivity, selectivity, and low consumption of power, making them ideal for use in portable and wearable devices [1, 2].

These devices have been at the forefront of multiple domains of the industry (Fig. 1) and have become an indispensable part of modern life due to their portability and ease of use. However, to achieve the innovation of next-generation devices, there is a need to understand the underlying rational design for deciphering the material interactions and also tuning material properties [2]. Optoelectronics is the study of detecting light-emitting devices that generate an electrical impulse when light falls on their active area. They have been an emerging technology that utilizes electronic appliances to detect, source, and control light. Optoelectronic devices such as solar cells (SCs), light-emitting diodes (LEDs), and laser diodes. These devices have been grabbing widespread attention due to their widespread implementation, but possess limited conductivity. Hence, there is a need to improve their functional properties. To achieve this, several attempts have been made, which have revealed several previously unknown characteristics such as optoelectronic and catalytic switching. However, rational designing of optoelectronic sensing devices is still a challenge.

An exciting and emerging field of study is nanotechnology, the applicability of nanoparticles (NPs) has been demonstrated in absolutely every domain of science. Although, many significant breakthroughs in material sciences and nanotechnology, commercial and industrial applications remain elusive. Advances in optoelectronic devices are also leaping commercial devices. The leaping research for commercial devices could be resolved by the integration of NPs and optoelectronics. Wide applications of polymers owe to their characteristic properties such as corrosion resistance, lower specific gravity, and many others. However, their drawbacks, such

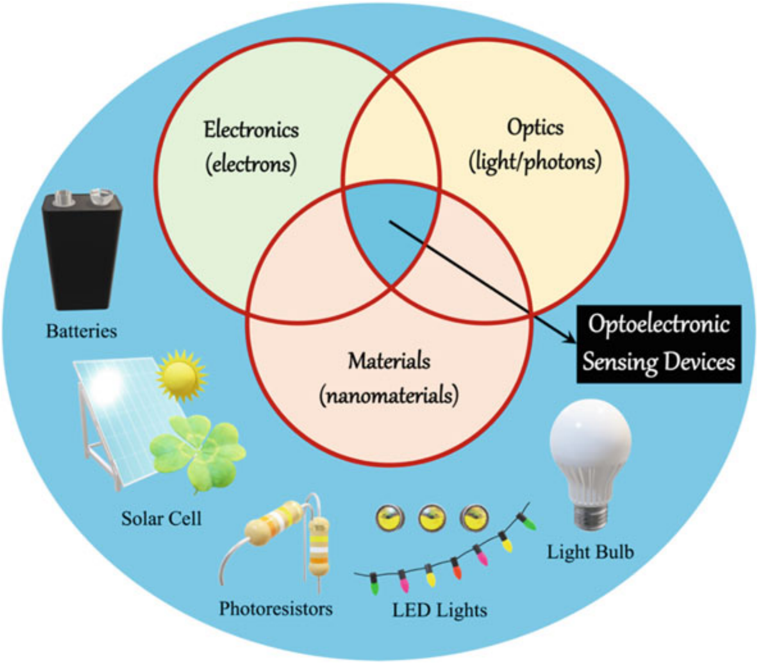

Fig. 1 Schematic representation of optoelectronic sensing devices: branch of study and applications

as low mechanical and thermal stability, limit their usage in constructing optoelectronic devices. Combining metals with polymers could overcome these limitations and exhibit advantageous features of parent material to the metallopolymer device. Polymeric nanomaterials (NMs) are utilized as building blocks in optoelectronic devices, and recent literature envisaged their wide range of applications including conversation and storage of energy, sensors, solar cells, and even biomedical.

One of the main factors that facilitate the advancement of optoelectronic sensors is the use of advanced NMs, including metallopolymer NMs. Metallopolymers are hybrid materials consisting of organic polymers and metal ions. The distinct characteristics of these materials result from the amalgamation of the mechanical properties of polymers with electronic and optical features of metal. Metallopolymer NMs have been widely researched because of their potential uses in optoelectronic sensing. Numerous methods have been developed, including electropolymerization, thermal polymerization, self-assembled coordination polymers, and ring-opening metathesis polymerization. These methods allow for the production of metallopolymer NMs with controlled size, shape, and composition, which can be tailored for specific applications [1]. Additionally, approaches such as top-down and bottom-up are implemented for the fabrication of devices with the desired structure and functionality, and the integration of these devices into larger systems. The use of metallopolymer NMs in optoelectronic sensors has several advantages, including high sensitivity, selectivity, and stability. These can also be easily integrated into different sensor platforms and offer a high degree of tunability, enabling the fabrication of sensors with improved performance [1].

The following book chapter provides a detailed description of the mechanistic approach behind optoelectronic devices. So far, optoelectronic devices could be of various types, and all of those are argued. Fabrication of metallopolymer NMs occurs via several methods and some of those have been described. Additionally, recent advances associated with metallopolymer NM optoelectronic sensing devices have been consolidated. The obstacles impeding research have been identified, and futuristic research opportunities have also been mentioned. The concluding remarks summarize the bright future of metallopolymer NM optoelectronic sensing devices, which have the potential to revolutionize the twenty-first century.

2 Optoelectronic Devices: Mechanism and Types

Optoelectronic devices are electronic devices that can sense, generate, and control light. They have revolutionized several industries, including healthcare, telecommunications, and renewable energy. This section of the chapter aims to give a detailed explanation of the mechanisms and various types of optoelectronic devices. By having a better understanding of these devices optimal methods can be determined to incorporate metallopolymer NMs into these devices and enhance their sensing capabilities.

Optoelectronic devices operate by converting light energy into electrical energy or vice versa, and their mechanisms are based on this principle. The fundamental or basic working principle underlying optoelectronic devices is photovoltaic, which involves the interaction of photons with matter. The photovoltaic mechanism encompasses the ejection of electrons from the material's surface by photons. The band gap value differs for every material. Electrons in the crystal lattice of a material can absorb the energy of photons when the photon energy is higher than the band gap value of the material. Absorbing this energy, electrons are ejected from the material's lattice. The photovoltaic mechanisms are commonly used in solar cells, photodetectors, and phototransistors. Additionally, different types of optoelectronic devices are also explored, namely, LEDs, organic LEDs (OLEDs), and diodes. These devices are used in display technologies, medical treatments, and data communication. All of these are briefly highlighted below.

2.1 Photodiodes

Photodiodes are utilized in a broad range of scientific and engineering uses due to their ability to convert light into electrical signals. It is a dynamic p–n junction. Upon irradiation of light onto the junction, current or voltage generates. The p–n junction operates in reverse bias. Upon irradiation with photon energy, electrons and hole pairs are created on the material's surface. Then diffusion of electrons to the junction occurs to form an electric field. They are used in three modes: photovoltaic as a solar cell, as an LED when forward-biased, and as a photodetector when reverse-biased. Photodiodes find applications in cameras, communication devices, industrial appliances, medical instruments, and others. For instance, a photodiode is utilized as a high-speed signal detector in a compression system for photonic analog-to-digital conversion. Herein, the bandwidth is 25 GHz and a sampling rate of 100 GHz to detect the input signal and convert it into a digital output signal [3]. Similarly, in a recent study by Zhang et al., photodiode is used as a photodetector for UV light. In this, a compact and high sensitivity UV photodetector was developed using a ZnO/Ga heterojunction. The photodetector showed a quick response time of 175 μs and a photo detectivity of 217 A W^{-1}, 4.57×10^{12} Jones [4].

2.2 Solar Cells

SCs are often referred to as photovoltaics, which are electronic devices that can directly convert solar energy into electric energy. They have gained popularity in diverse fields of science and engineering because they can produce clean and sustainable energy. On irradiation of sunlight on a SC, current and voltage simultaneously produce electric power. These photons from sunlight irradiate the silicon atoms in the solar cell for energy transfer to take place for the loss of electrons. Two layers constitute the solar cell where the first layer is the main source of electrons. The electrons from the first layer jump to the second layer. No primary fuel supply is required by SCs. They found diverse applications in electrification in rural areas, telecommunications, remote monitoring, and many more. For example, in a report, a single-crystalline Si wafer was utilized to produce SCs with 18.8% efficiency. The findings indicate that solar cells can perform exceptionally well in regards to parameters such as open-circuit voltage, short-circuit current, and fill factor [5]. Another study presented the development of perovskite SCs with improved efficiency. The researchers employed ZnO nanostructures as a layer for transporting electrons (ETL). According to the findings, incorporating ZnO-NN as an ETL has a positive impact on the absorption of light, charge separation, and transport of charge in the SCs, resulting in an enhancement from 4.51 to 6.77% and a fill factor from 67.60 to 44.28%, and density of current from 21.07 to 20.56 mA cm^{-2} [6]. In addition, SCs have been used in various applications, including remote monitoring and electrification in rural areas. In this, Sharma et al. presented the design and simulation of a solar-powered wireless sensor network for remote monitoring. SCs are utilized to power the wireless sensor network and demonstrated that the network could provide reliable and efficient remote monitoring for various applications, including environmental monitoring and structural health monitoring [7].

2.3 LEDs

An LED is a diode made of a heavily doped p–n semiconductor, which is operated in forward bias. It emits disordered light in narrow-spectrum when electrically forward-biased. Electroluminescence is the phenomenon where the recombination of electrons and holes from the n- to p-side of a semiconductor diode, respectively, results in the emission of photons. Photons produce light where the light color is decided by the band gap energy of the semiconductor diode. The intensity of emitted light is proportional to the current magnitude. Since LED works in forward biasing, the reverse voltage must be kept low and the device must be protected against it. LEDs produce less heat while consuming less power, justifying their advantage over incandescent lamps. For example, gallium nitride (GaN) layer was utilized to produce LEDs with an efficiency of 75% at high current densities. The findings indicated that the incorporation of a GaN layer could increase the rate of radiative recombination and reduce the rate of non-radiative recombination in LED, leading to an enhancement of the efficiency [8]. Another study utilizes colloidal QDs as the active layer in the LED and demonstrated that the QDs could effectively improve the efficiency and color purity. The results showed that the LED had an external 7.5% quantum efficiency and a peak wavelength of 455 nm [9, 10]. In addition, LEDs, have been used in various applications, including solid-state lighting and display technologies.

2.4 Optical Fiber

These are the plastic or glass-made transparent fibers functioning as a waveguide to facilitate the transfer of light between two ends of the light pipe. Core, cladding, and jacket are the three concentric layers that constitute the optical fibers. The core is the central silica-made section of the fiber which acts as the light-transmitting region. To protect the core, cladding is the protective layer around it that limits the light by total reflection at the core-cladding interface. Hence cladding is the optical waveguide made of silica around the core. To further protect the core and cladding from any physical damage, a non-optical layer called a jacket consisting of one or more polymeric layers is induced. Different colors of jackets indicate different fiber-optic cables. In single-mode fiber, light propagates straight through the cable while in multimode cable, light propagates through different modes. For example, suspended-core optical fiber method is utilized to monitor fluid density in real-time. The potential of using this was demonstrated for applications such as chemical analysis and process control [11]. This study demonstrated a fiber optic temperature sensor that can withstand harsh environments such as high temperatures and corrosive gases. Further, the potential of using this sensor for industrial applications such as monitoring of chemical processes and power plants was also demonstrated [12].

2.5 *Laser Diodes*

With a similar operating principle to LEDs, laser diodes are devices that transform electrical energy to light energy. Laser diodes are an extensive source of highly monochromatic, coherent, and directional light. They produce stimulated emissions resulting in higher generation efficiency. The population inversion of the electrons is induced when a voltage is supplied across the p–n junction, and the semiconductor area then becomes accessible for the laser beam. Since the ends of the p–n junction in the laser diode are polished, the photons that are released bounces back, producing additional electron pairs. The new photons will therefore be in phase with the ones that came before them. They found applications in optical fiber communications, optical memories, military applications, surgical procedures, etc.

Overall, this section aims to provide a foundational understanding of optoelectronic devices, which is crucial in the development of metallopolymer NM-based optoelectronic sensors. By understanding the mechanisms and types of optoelectronic devices, researchers can identify the best approaches for integrating metallopolymer NMs into these devices for enhanced sensing capabilities.

3 Fabrication of Optoelectronic Devices

The formulation of optoelectronic devices involves the design, fabrication, and assembly of materials with both electronic and optical features. Optoelectronic devices are commonly used in various applications, including displays, sensors, photovoltaics, and communication devices. The fabrication involves several steps, including the selection of appropriate materials, the fabrication of devices with the desired structure and functionality, and the integration of these devices into larger systems. It can be classified into two main approaches, namely top-down and bottom-up fabrication. Firstly, top-down fabrication involves the fabrication of devices through traditional lithographic approaches, like photolithography and electron beam lithography. In this, devices are fabricated by carving out a bulk material to form the desired structure. It allows the creating of highly uniform devices with precise control over their size and shape. Secondly, bottom-up approach involves the assembly of devices through self-assembly or chemical synthesis techniques. In this, materials are synthesized or grown to form the desired structure through chemical reactions. This approach offers several advantages, such as the ability to create highly ordered structures with controlled dimensions at the nanoscale level.

Optoelectronic devices can be fabricated using a plethora of materials, such as organic, inorganic, and hybrid materials. Organic materials, such as polymers, are attractive for such devices because of flexibility and low-cost fabrication. Inorganic materials, such as silicon and gallium nitride, offer excellent electronic and optical properties, making them ideal for high-performance devices. A brief exploration of the synthesis approaches that fall under top-down or bottom-up approach, including, Hummer's, chemical vapor deposition (CVD), sol–gel, liquid exfoliation, and other are highlighted.

3.1 Hummer's Method

It is a commonly used technique for synthesizing graphene oxide (GO) and other metallopolymer nanomaterials (NMs). GO is one of the important 2-dimensional (2D) materials for optoelectronic devices. The process includes the use of potassium permanganate, concentrated sulfuric acid, and sodium nitrate to oxidize graphite. However, modifications are being proposed by researchers to replace the conventional Hummer's method to produce a quantity of GO replacing $NaNO_3$ [13–15]. The resulting GO can be further functionalized and used in the development of optoelectronic devices. For example, GO by oxidation of graphite was successfully synthesized using Hummer's method. Then, GO was functionalized with a poly[2-(3-thienyl)-imidazole[4,5-f][1,10[phenanthroline Ru(II) hexafluorophosphate], to produce a composite. The resulting composite showed excellent photoresponse behavior with a fast response and recovery, along with high sensitivity to light. The study demonstrated the potential of using the Hummer's method for the synthesis of metallopolymer NM-based optoelectronic devices.

3.2 Liquid Exfoliation

It is a bottom-up approach for the designing of metallopolymer NMs that involves the dispersion of layered materials in a solvent followed by exfoliation to obtain 2D nanosheets. This is the method of conversion of multi-layered 2D materials into mono- or few-layered materials. The conversion is made possible by overcoming the van der Waals forces between the layers. The exfoliation is carried out by several different methods such as ultrasonication, shear exfoliation, and electrochemical exfoliation [16, 17]. The exfoliated nanosheets are then functionalized with metal ions or polymers to produce metallopolymer NMs. This offers a scalable and cost-effective route for the construction of metallopolymer NMs with tenable properties for optoelectronic devices [18]. For instance, in a study by Kim et al., liquid exfoliation of MoS_2 was used to produce metallopolymer NMs that exhibit high photoresponsivity for photodetection applications [19].

3.3 Chemical Vapor Deposition (CVD)

This method is employed to apply a thin layer of materials onto a surface. It involves the use of a vapor phase precursor, which is decomposed on the substrate to produce a solid film, resulting in multi-layered 2D materials to fabricate optoelectronic devices. Bilgin et al. proposed the synthesis of mono- or few-layered MoS_2 structures by direct vapor phase sulfurization of MoO_2 (precursor) using CVD [20].

3.4 Physical Vapor Deposition (PVD)

A thin film of material is deposited onto a substrate using physical means, such as sputtering or evaporation. In a recent study, a ZnO nanorod array was synthesized using PVD and then coated with a conducting polymer to fabricate a high-performance UV photodetector. Similarly, PVD was also used to deposit Ag and then electrochemically polymerized a conducting polymer onto the Ag film to produce a metallopolymer-based UV photodetector with high responsivity.

3.5 Wet Chemical Method

This method consists of sol–gel, hydrothermal, and co-precipitation synthesis. It involves chemical reactions among the reactive precursor solutions. Elsayed et al. proposed the synthesis of $Cd_{1-x}Nd_xSe$ ($0 \leq x \leq 0.09$) nanocrystalline quantum dots (QDs) by wet chemical approach and suggested their potential applications in optoelectronic devices [21].

3.6 Sol–Gel Method

It is utilized to synthesize inorganic materials where a sol, which is a liquid colloidal suspension of solid particles, is formed and then subjected to gelation, resulting in the formation of a 3D network of solid particles. For example, TiO_2 NPs were synthesized via sol–gel method and then incorporated them into a conducting polymer matrix to fabricate a metallopolymer-based UV photodetector with high sensitivity and stability. Similarly, SnO_2 NPs were synthesized and then mixed with a conducting polymer to produce a metallopolymer-based gas sensor for detecting NH_3 with high sensitivity.

3.7 Electrochemical Deposition (ECD)

This technique involves the deposition of a metal or metal oxide film onto a substrate using an electrochemical reaction. For example, Au NPs were deposited onto a conducting polymer film using ECD and then used the resulting metallopolymer to fabricate a high-performance flexible strain sensor. Similarly, Fe_3O_4 NPs were electrodeposited onto a conducting polymer film to produce a metallopolymer-based magnetic sensor with high sensitivity and selectivity.

3.8 Spin Coating

This technique involves the deposition of a thin layer of material onto a surface by spinning the substrate at high speeds while the material is applied. For example, a conducting polymer solution was spin-coated onto a Si substrate and then deposited Cu using PVD to produce a metallopolymer-based flexible thermoelectric generator with high power output. Similarly, CdS QDs were spin-coated onto a conducting polymer film to fabricate a metallopolymer-based photodetector with better sensitivity and selectivity. The choice of techniques depends on the specific requirements of the device and the materials used. The selection of appropriate materials is critical for achieving the desired electronic and optical properties. The integration of these devices into larger systems is also essential for their practical application. The advancement of new fabrication strategies and materials is an active area of research, with the potential to revolutionize the field of optoelectronics.

4 Synthesis of Nanostructured Metallopolymer

Nanostructured metallopolymers are materials that have a network structure with nanoscale dimensions, composed of monomers that contain metal and are polymerized. Due to their distinctive properties, such materials have attracted considerable attention as potential candidates for optoelectronic sensing device development. These materials have been extensively studied for the development of the new and rational design of optoelectronic sensing devices. There are several synthetic methods that can be used to fabricate metallopolymer NM with nanoscale dimensions. This subsection comprises a brief discussion on few of those synthetic approaches for the polymerization of metal-containing monomers. It is a straightforward method, in which, monomers containing metal ions or metal complexes are polymerized using a variety of techniques, including electropolymerization (EP), thermal polymerization, self-assembly coordination polymers, and ring-opening metathesis polymerization (ROMP). Further, it enables accurate manipulation of the size, shape, and chemical makeup of the resulting metallopolymers.

4.1 Electro Polymerization (EP)

In this process, a polymer coating deposits onto the surface of electrode with the help of an applied potential to begin the substrate polymerization. This type of thin film synthesis requires higher monomer solubility in the electrolytic solution, in situ the polymeric film is developed on the electrode solution [22]. Both oxidative and reductive EPs are feasible with suitable functional groups, such as pyrrole, thiophene, vinyl groups, and triphenylamine [23–25]. The obtained film has better stability, adhesion, and electrical connectivity with the surface of the electrode. Moreover, the extent and thickness of the film surface are easily maintained with different polymerization spans [25]. Nie et al. fabricated a phen-1,4-diyl-bridged tris-bidentate di-Ru complex. The metallopolymer thin film of ruthenium (Ru) complex deposits onto the surface of Pt and ITO through reductive EP [26].

Moreover, Yao et al. bridged a biscyclometalated Ru complex connected by the 2,7-deprotonated version of 1,3,6,8-*tetra*(2-pyridyl)pyrene and the resultant metallopolymer was deposited onto the surface of ITO electrode via EP process [27]. Bao et al. prepared $[Fe(L)_2]$ $(PF_6)_2$, where L = 4′-{[p-(*N*-butyl-*N*-phenyl)amino]-phenyl}-2,2′:6′,2″-terpyridine, using an oxidative EP. This involved repeatedly cycling the potential of the working electrode between 0 and 1.8 V in a solution of Bu_4NClO_4/CH_3CN (0.1 mol/L) containing a monomer concentration of 5.0×10^{-4} mol/L. The polymeric hybrid film exhibits outstanding stability in a solution without the presence of a monomer and has a non-diffusional transfer of charge tendency of the Fe(III)/Fe(II) couple, as well as an irreversible redox change in phenylamine species on the working electrode of Pt. Electrodeposition was used to create a film containing metal centers by depositing a Fe(II)-terpyridine complex functionalized with acrylamide onto ITO. This exhibits a distinct electrochromic characteristic of pale yellow from purple as in Fig. 2 [28].

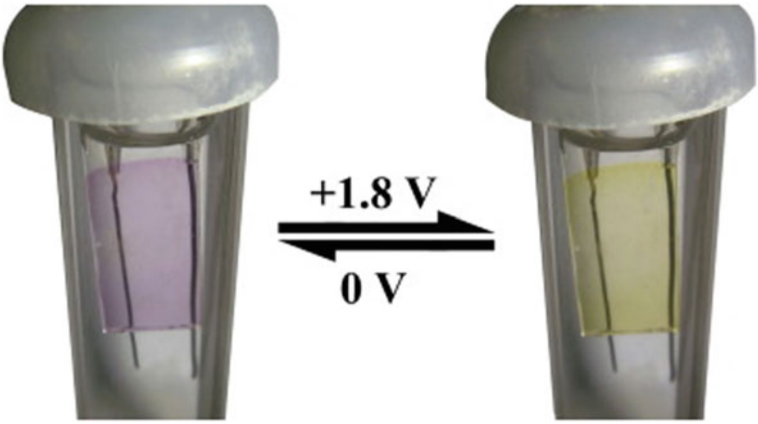

Fig. 2 The film of acrylamide functionalized Fe(II)-terpyridine complex showing electrochromic characteristics. Adapted with permission from [28]. Copyright (2013) Elsevier

4.2 Thermal Polymerization (TP)

In thermal polymerization (TP), neither photo-initiators nor added reagents are required for the initial polymerization of vinyl-substituted monomers [29]. Mayo et al. proposed a mechanism that includes the polymerization of styrene and vinyl derivatives in the initiation step leads to the spontaneous generation of free radical species, which forms polymers and a network of polymers [30]. The electrochemical polymerization of monomers that contain acrylate groups can be challenging because they are electrically distant from the aromatic rings. However, TP is a beneficial tool for this type of molecule [31]. Thin film of Ru(II) complexes that contain bipyridine ligands have been synthesized using TP [32]. Elloitt et al. thermally polymerized a monomer tris(5,5′-dicarbo(3-acrylatoprop-1-oxy)-2,2′-bipyridine)Ru(II) complex to form a metallopolymer. During the synthesis of metallopolymer, the p-toluene sulfonate species of monomer complex was spin-coated onto the SnO_2 surface. The monomer has six acrylate species that enhanced the stability by the formation of a highly cross-linked structure due to TP [31].

4.3 Self-Assembled Coordination Polymers (SACP)

Coordination wires are 1D materials developed by self-assembly, where metal ions coordinate with ligands like bis(terpyridine) that have two binding subunits. This results in the formation of chains of metallopolymers [33, 34]. Coordination nanosheets are formed by self-assembly, with ligand utilization along with metal ions in the complexation reaction is branched, such as tris(terpyridine) [35]. Metallopolymers developed in this manner have distinctive colors attributed to metal to charge transfer of ligand. They also exhibit metal-based redox process in cyclic voltammetry studies, resulting in a shift in color to the visible region [36]. Hsu et al. formed a Co(II)-based metallo-supramolecular polymer (polyCo) film by the SACP of Co(II) ion. Moreover, polyCo, based on bisterpyridine self-assembly developed through spray casting of polymer onto ITO electrode surface. This process results in the production of a high quality film polymer [37]. Moreover, Pai et al. fabricated metallo-supramolecular polymers of Co(II), Fe(II), and Ru(II) metals via self-assembling from rigid, π-conjugated bis-terpyridine molecules having various linker numbers. The switching reversibility and stability were enhanced after the introduction of pyridine linkers [34].

4.4 Ring-Opening Metathesis Polymerization

An effective technique for fabricating well-defined polymers with exact molecular weight and intricate topologies is ring-opening metathesis polymerization (ROMP)

[38]. Through ROMP, cyclic olefins transform into polymers of unsaturated main chain. Polymers having a metal center as the main chain as well as side-group desirable structure as functional soft materials due to their potential applications [39]. ROMP reactions utilize strained metallocenophanes and their derivatives with relevant C_x ($x = 4$ to 7) π-hydrocarbon as monomers to produce metal-containing polymers with metal centers of s molecular weight [40]. The tilt angle is correlated with the ring opening, which is driven by the strain in the monomer, along with other structural factors [41]. Grubbs catalysts such as Mo and Ru complex are used as catalysts in the ROMP process [42]. A popular cyclic olefin, norbornene, is utilized in ROMP, which is easily functionalized by sizable, chemically powerful organic or inorganic compounds. By post-modification, polynorbornenes with sidechains containing functional groups could be further bonded to other metals or metal complexes [43]. Mayer et al. prepared the first paramagnetic and neutral [n]cobaltocenophanes $Co(\eta^5\text{-}C_5H_4)_2(CH_2)_3$ and $Co(\eta^5\text{-}C_5H_4)_2(CH_2)_2$ by the reaction of appropriate ligand precursor and cobalt chloride in tetrahydrofuran. In contrast to [3] cobaltocenophane, which is just slightly deformed, the [2] cobaltocenophane exhibits significant distortion from metallocene-type geometry and is hence extremely strained. In the presence of ambient oxygen, both are easily oxidized with NH_4Cl to produce the equivalent cationic [n] cobaltocenophane salts [44]. Similarly, Baljak et al. synthesized strained dicarba [2] nickelocenophane by $NiCl_2$ and $Li_2[(C_5H_4)_2(CH_2)_3]$ in tetrahydrofuran [45]. Adams et al. uses an optimal methodology for trovacene dilithiation that further isolates a high yield of $[V(\eta^5\text{-}C_5H_4Li)(\eta^7\text{-}C_7H_6Li)]\cdot$PMDTA. In solid state, it has a dimeric structure with distinct lithium environments, a) two Li atoms are terminally attached to a C_5H_4 species and further stabilized by a PMDTA ligand via the coordination bond, and b) took up a position on a bridge site amidst the sandwich segments and demonstrated a deformed trigonal-planar structure. The [1] sila- and [1] germatrovacenophanes as well as [2] stannatrovacenophae were produced when $[V(\eta^5\text{-}C_5H_4Li)(\eta^7\text{-}C_7H_6Li)]\cdot$PMDTA reacted with the suitable dihalide compound [46].

In summary, the fabrication of nanostructured metallopolymer can be achieved via several synthetic methods. These methods offer precise control over the size, shape, and composition of the resulting metallopolymer NMs, making them suitable for use.

5 Reinforcing Properties of Nanostructured Metallopolymer

Metallopolymers have been reported with exciting applications with a combination of properties emerging from technological advancements of polymers and the functionality of metal centers. When these metallopolymers are taken to the nanoscale, they emerge as nanostructured metallopolymers, which are utilized in portable optoelectronic devices as sensors. With these reinforcing properties, nanostructured metallopolymers find profound applications as biocatalysts, electroactive, photoactive, functional materials, and so on. The most important properties have been briefly discussed below.

5.1 Tunability

Polymeric NMs exhibit discerning light absorption owing to their tunable band gap. Selectivity towards wavelength is an outcome of the interaction between metal and ligand. This characteristic property of tunability finds diverse applications of metallopolymers in many domains that include camera, mimicking human eye devices, and so on. Tunability-based photophysical features and applications in electronics and photonics have been summarized in the literature [47]. Metal–Ligand interaction plays a pivotal role in controlling stiffness, strength, thermodynamic stability, and other mechanical properties of the metallopolymer. In a metallopolymer, nickel carboxylate was used as a tunable cross-linking interaction by Vidavsky et al. In this study, several neutral ligands were used to alter the ionic interaction to tune mechanical characteristics, hence justifying the role of ligands in the novel design of tunable nanostructured metallopolymers [48]. Ln-containing metallopolymers have been reported to emit tunable multicolored photoluminescence and white light emission [49]. Tunable optoelectronic and electro-chromic properties of metallopolymers contribute towards efficient and compact microenergy storage systems [50].

5.2 Carrier Mobility and Stability

Metallopolymers are known for their enhanced charge transport properties. In conjugated materials, the interaction between metal and ligand contributes to the transfer of charge carriers. As investigated through the fabrication of transistor devices, Fe(III) containing metallopolymer exhibits high charge carrier mobility. Initially, the polymer possesses 0.96 $cm^2\ V^{-1}\ s^{-1}$ mobility of charge carrier while after Fe coordination, an improvement of two-fold in carrier mobility was observed. This study presents how the performance of the device is affected by the metal center present in the polymer's ligand [51]. The addition of metal elements to polymers can also enhance their thermal stability. The metal centers can act as heat sinks, dissipating heat and preventing thermal degradation of the polymer network. Nanostructured metallopolymers can exhibit even higher thermal stability due to their nanoscale dimensions, which can inhibit the propagation of thermal degradation.

5.3 Light Absorption Behavior

The light absorption capability of a photovoltaic device is a crucial factor that determines its efficiency. Nanostructured metallopolymers tend to absorb continuous solar spectrum with a wavelength lower or higher than the band gap. The sensitivity of optical signals is reliant on the interaction of photons with metallopolymer NMs. The applications of nanostructured optoelectronic appliances like solar cells, LEDs, and photodetectors work on the generation of electrons and photons upon light absorption. Attributed to the light absorption tendency exhibited by metallopolymers, they serve as energy storage devices in the form of organic batteries, energy-generating devices in organic solar cells, and energy-saving devices in organic LEDs. For instance, Ru-based metallopolymer integrated on reduced graphene oxide (rGO) has been utilized as an efficient hybrid harvester in solar cells [52].

5.4 Doping

The doping of NMs can significantly affect the sensing performance of optoelectronic sensors. Doping can introduce impurities into the NMs, which can modify their electrical, optical, and chemical properties, leading to improved or enhanced sensing performance. Conducting polymers with different doped NMs end in excellent products as they have combined properties comprising of unique catalytic properties of each dopant towards different targets [53–55]. For instance, Zamiri et al. investigated how the dielectric and optical characteristics of ZnO are affected by doping, which possesses potential applications on optoelectronic devices. Mg doping results in an elevation of defects in grain's boundary reflecting high dielectric constant [56]. Ma et al. summarized how doping strategies of conductive polymer hydrogels improve different sensing performances including sensitivity, stability, and selectivity [57]. For example, SnO_2 NPs were doped into a metallopolymer of poly(3-hexylthiophene-2,5-diyl) (P3HT), leading to a significant improvement in the sensing performance for NO_2 gas [58]. Similarly, in a study by Verma et al., the doping of GO into a P3HT metallopolymer has been shown to significantly improve the photoresponsivity of the resulting photodetector [59]. The improved sensing performance can be explained by the raised exposed surface and better charge transport that is provided by the doping NMs. In addition, doping can also alter the bandgap of NMs, which can affect their optical properties. This modification can lead to improved light absorption and emission, making them suitable for optoelectronic applications like solar cells, LEDs, and photodetectors. Overall, the choice of the type of NM and the doping element depends on the specific sensing application and the desired performance parameters.

5.5 Electrical and Optical Parameters

Nanostructured metallopolymers can exhibit unique features because of the presence of metal centers in the polymer network. The metal centers can impart specific electronic properties to the polymer, such as increased conductivity or enhanced charge transport. Additionally, the metal centers can exhibit unique optical properties, such as fluorescence or phosphorescence, which can be exploited in optoelectronic devices.

5.6 Catalytic Activity

Nanostructured metallopolymers can exhibit catalytic activity due to the existence of metal centers. They can be used as biocatalysts or electrocatalysts in a plethora of areas, such as fuel cells or biosensors. The nanoscale dimensions of these materials can further enhance their catalytic activity by increasing their surface area and exposing more catalytic sites.

In summary, these properties make nanostructured metallopolymers attractive for various applications such as optoelectronic devices. They require a careful selection of nanostructures that devices depend on different factors such as the intended use and the specific properties of the device. Different types of nanostructures, such as nanowires, nanotubes, nanoparticles, and nanosheets, have been explored for optoelectronic sensing devices, and each has its advantages and limitations. For instance, nanowires and nanotubes offer high sensitivity and low detection limits due to their large surface-to-volume ratios. In contrast, NPs provide a straightforward method for synthesis and adjustable characteristics, making them appealing for a wide range of uses. In contrast, nanosheets, including graphene. Possess distinct features that make them potential candidates. For example, Fan et al. developed a polymeric SC with a power conversion efficiency (PCE) of 11.9%, V_{oc} of 0.97 V, and J_{sc} of 17.8 mA cm^{-2}. Further, they investigated the effect of film thickness on PCE and found that it was 11.3% at 255 nm from 11.9% at 150 nm. The weight ratio of the donor–acceptor components had a significant impact on the performance of the SC. The metallopolymeric SC showed a fill factor between 64 and 69%, constant V_{oc} between 0.96 to 0.97, and variable J_{sc} between 15.9 and 17.8 mA cm^{-2}. In the 300–790 nm range, they achieved an external quantum efficiency (QE) of 81.1% [60]. The photovoltaic device demonstrated a PCE of 1.33%, V_{oc} of 0.62 V, and J_{sc} of 3 mA cm^{-2} along a fill factor of 0.66. They used a variety of fabrication circumstances, such as varied ratios of the active material's components [61]. Therefore, there is no one-size-fits-all answer to which type of nanostructure is best for the development of optoelectronic sensing devices. The choice of nanostructure depends on the specific application and the desired properties of the device.

6 Optoelectronic Sensing Applications of Metallopolymer Nanomaterials

To strengthen present-day technologies, novel rational designs to innovate optoelectronic sensing devices should be adopted by the scientific community. Based on the recent advancements and the above discussion, metallopolymer-based optoelectronic sensing devices should be the futuristic solution to develop next-generation devices. The following discussion will briefly demonstrate metallopolymer-based optoelectronic sensing devices in various applications such as energy conservation, photodetectors, and other sensors.

6.1 Energy Devices

As we know, the world today faces a huge energy crisis owing to the rapid industrialization and use of day-to-day devices. Therefore, it emphasizes that new ways must be adopted for energy conservation and storage. For many decades, natural sources for energy conservation such as fossil fuels are been popularly used. However, natural sources are not sufficient to overcome the present age's energy requirements. To combat that, several ways have been adopted over the past decades such as photocatalysis, solar cells, perovskites, electrochemical cells, and many more. They have their limitations and therefore, the intervention of nanotechnology for developing new energy devices has been of immense interest to researchers. With that note, a promising approach of utilizing metallopolymer optoelectronic devices has grabbed attention. In this section, a brief outlook on the fabrication of metallopolymer-based energy devices has been provided.

Light-emitting electrochemical cells (LECs), which are derived using metallopolymer emerged as a new device with tunable properties, i.e., the polymer can rearrange under different conditions such as temperature, etc. These exhibit different emission wavelengths at an applied voltage [62]. Other than LECs, another interesting class of metallopolymer optoelectronic sensing devices is solar cells. They offer huge potential considering the ongoing energy crisis. Vinoth et al. have synthesized a polymer solar cell, in which they complexed polyaniline (PANI) and Ru with the help of pyridyl benzimidazole. Then, the PANI-Ru complex was grafted onto rGO nanosheets via covalent attachment. Figure 3 demonstrates the synthesis of PANI-Ru@rGO nanosheets. Further analysis demonstrated that the PANI-Ru exhibits properties of an electron donor and therefore, enhances the performance of polymer solar cell devices [52].

A work conducted by Gopinath et al. illustrates the synthesis of the dye-sensitized solar cell (DSSC) by exploring metallopolymers. In a typical synthesis, the phenanthroline-Ru metallopolymer complex was orchestrated via the atom transfer radical polymerization (ATRP) process. These were self-assembled in thin film nanostructures (temperature-assisted anisotropic), which form a uniform micelle

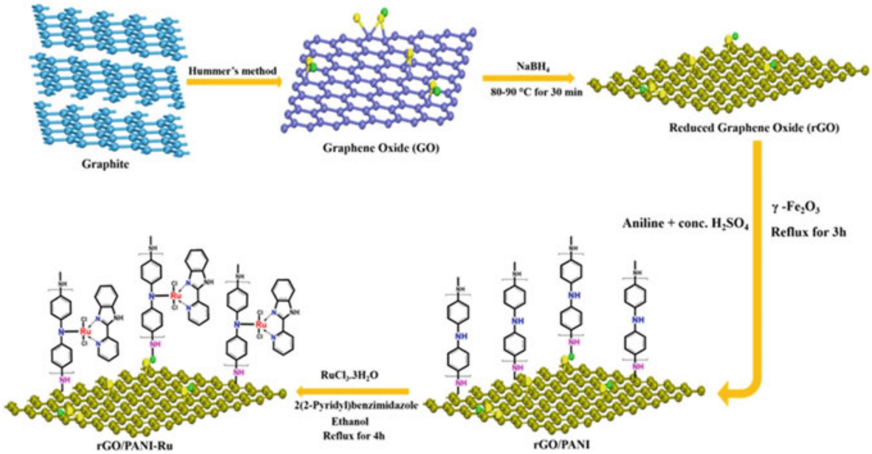

Fig. 3 Synthesis of PANI-Ru@rGO nanosheets. Adapted with permission from [52]. Copyright (2017) Springer Nature

in nano-dimensions. These metallopolymer-based DSSCs devices have additional liquid electrolyte components as well as improved performance for energy harvest action [63].

A recent study explores the conjugation of PANI with ZnS nanosheets, which not only enhances its performance but also makes the metallopolymer flexible and environment-friendly on substrates such as cellulose paper or cotton. The high photoresponsivity of ZnS-PANI devices is attributed to the interface between the metal and polymer. In addition, the paper- and cotton-based ZnS-PANI devices demonstrated ultrahigh photoresponsivity of 3.671 mA/W and 1.740 mA/W, respectively. This research work demonstrates the future implications of metallopolymer nanodevices that are tunable and eco-friendly [64].

6.2 *Sensors*

Sensors and actuators are also been demonstrated for several applications in various scientific areas. Sensors are devices that detect a specific kind of analyte such as humidity, gases, biomolecules, etc. There are several kinds of sensors that are known today, such as humidity sensors, gas sensors, temperature sensors, touch sensors, and many more [65–73]. The subsequent part of the text explores recent progress in the field of metallopolymer optoelectronic sensors.

Verma et al. have synthesized MoS_2 nanoflakes via ultrafiltration. Then, the nanoflakes were functionalized with acrylamide monomers using a polymerization approach. The synthesis of the MoS_2 nanoflakes with polyacrylamide (PAAm) is shown in Fig. 4 [74].

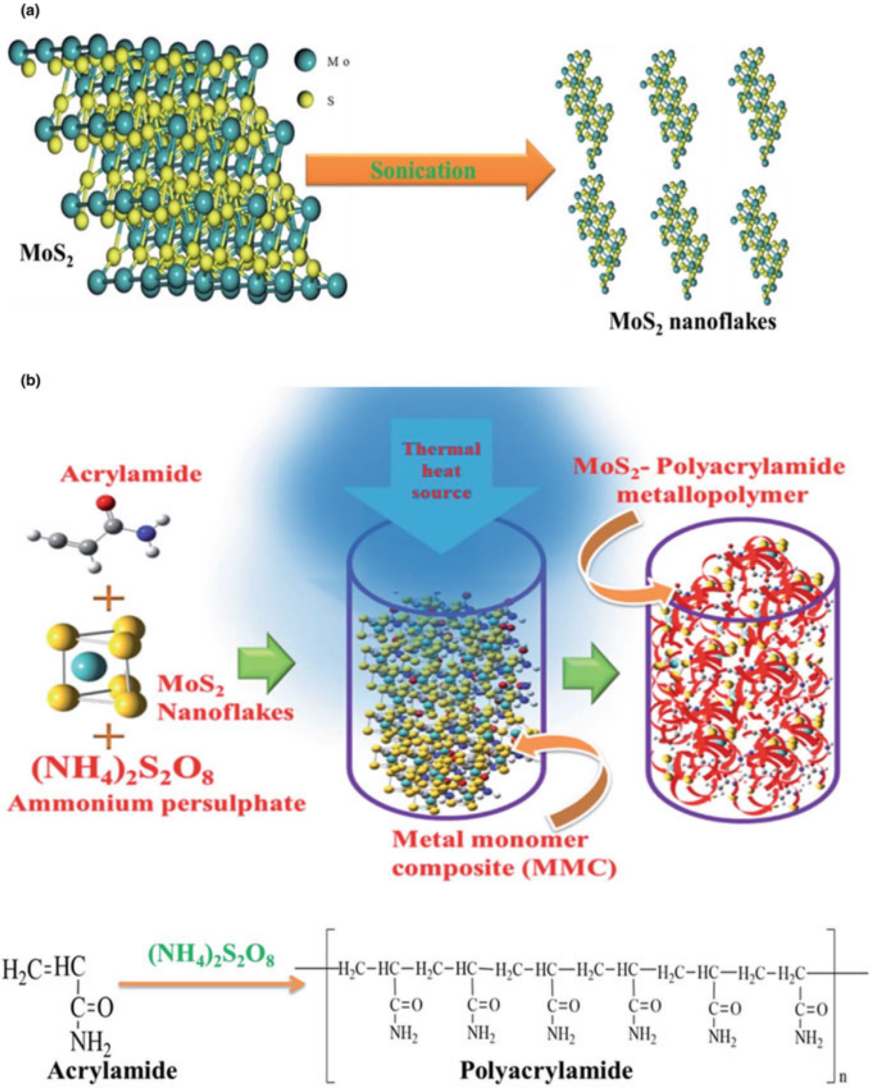

Fig. 4 Synthesis of MoS_2-polyacrylamide. **a** Formation of MoS_2 nanoflakes using ultrasonication. **b** Functionalization of MoS_2-polyacrylamide via polymerization. Adapted with permission from [74]. Copyright (2021) Royal Society of Chemistry

The research group of Verma et al. further characterized the synthesized metallopolymer nanostructure and demonstrated their potential application in photodetection transistors. The metallopolymer nanostructured energy devices, consisting of the Keithley meter, light source, and power meter, and the experimental setup are depicted in Fig. 5. Their characterization parameters were enhanced due to the

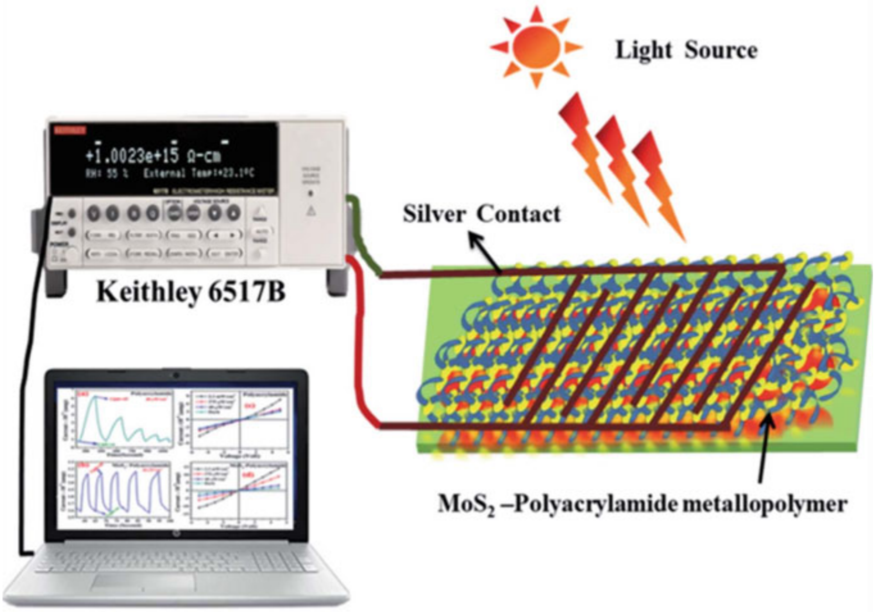

Fig. 5 Representation of the experimental setup of MoS_2-polyacrylamide photodetection transistor. Adapted with permission from [74]. Copyright (2021) Royal Society of Chemistry

interactions between metal and the polymer. Because the metallopolymer NMs offer a wide range of the spectrum. Therefore, the metallopolymer photodetector was successfully performed for photodetection [74].

Zhao et al. examined the prospects of an oxygen sensor, which was fabricated using two types of metals, i.e., Ru (oxygen-sensitive) and terbium (Tb) (oxygen-insensitive). These metals were separately complexed with a copolymer of bipyrimidine, thereby forming Ru-Poly and Tb-Poly, respectively. Further, the hydrophobicity of both these metallopolymers was exploited for the fabrication of a facile oxygen nanoprobe via the precipitation method (Fig. 6). In a typical synthesis, the following were added in the ratio of 7:3:2 Ru-Poly, Tb-Poly, and polystyrene-polyethylene glycol-COOH (PS-PEG-COOH). The resultant metallopolymer nanoprobes exhibit different emission wavelengths, i.e., 300 nm (red) and 460 nm (green), respectively. Herein, the reference used was green emissive Tb-Poly due to its stability, and red emissive Rb-Poly demonstrated enhanced dissolved oxygen quenching ability. Therefore, the metallopolymer nanoprobes were examined to successfully determine intercellular oxygen within tumor spheroids [75].

Naidji et al. developed films based on Ru-terpyridine metallopolymer via an electropolymerization approach. They utilized the Ru-terpyridine for ammonia gas detection up to 25 ppm at ambient temperature. Therefore, it opens new doors for the development of devices at ambient temperatures as most metallopolymer devices work well at high temperatures [76]. Yadav et al. showed the fabrication of a humidity

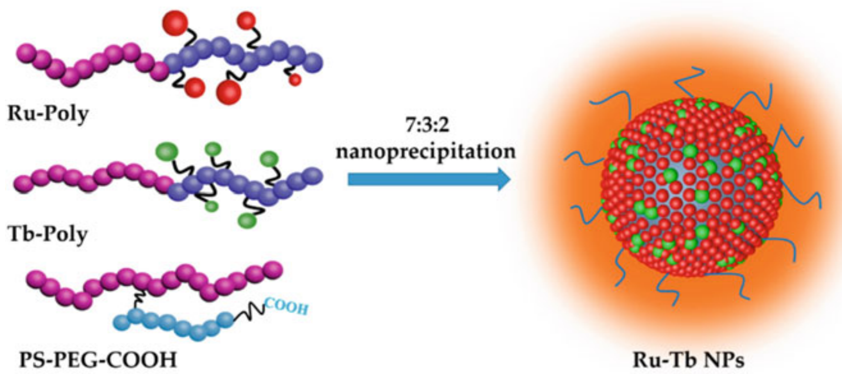

Fig. 6 Schematic representation of the synthesis of Ru-Tb-Poly NPs via nanoprecipitation method. Adapted with permission from [75]. Copyright (2019) MDPI

sensor using solid-state polymerization of PAAm with zinc (II) nitrate ($Zn(NO_3)_2$). The $Zn(NO_3)_2$-PAAm metallopolymer was deposited onto the borosilicate films. Then, they investigated the desorption/sorption of humidity onto the synthesized files, which were carried under room temperature. The humidity assessment showed improved sensitivity as well as a faster response time of 250 s, and a recovery time of 37 s. They repeated the experiment a couple of times and demonstrated stability of approximately 96% [77]. Chaudhary et al. also explored PAAm polymer for the development of humidity sensors. In their synthesis, copper (II) nitrate ($Cu(NO_3)_2$) was complexed with PAAm via solid-state polymerization. The homogenous transparent gels were prepared using the $Cu(NO_3)_2$-PAAm metallopolymer. The humidity assessment at room temperature was carried out and their results showed enhanced sensitivity with recovery and response times of 31 s and 76 s, respectively. Further, reproducibility was examined with negligible aging effect [77].

For example, Fan et al. developed a polymeric SC with a power conversion efficiency (PCE) of 11.9%, V_{oc} of 0.97 V, and J_{sc} of 17.8 mA cm^{-2}. Further, they investigated the effect of film thickness on PCE and found that it was 11.3% at 255 nm from 11.9% at 150 nm. The weight ratio of the donor–acceptor components had a significant impact on the performance of the SC. The metallopolymeric SC showed a fill factor between 64 and 69%, constant V_{oc} between 0.96 to 0.97, and variable J_{sc} between 15.9 and 17.8 mA cm^{-2}. In the 300–790 nm range, they achieved an external quantum efficiency (QE) of 81.1% [60]. The photovoltaic device demonstrated a PCE of 1.33%, V_{oc} of 0.62 V, and J_{sc} of 3 mA cm^{-2} along a fill factor of 0.66. They used a variety of fabrication circumstances, such as varied ratios of the active material's components [61]. Verma et al. synthesized metallopolymer nanohybrids of ZnS nanosheet in a polyaniline matrix that was used in photodetector. The nanohybrid showed the maximum responsivity of about 396.479 A W^{-1} at a drift potential of 86 V. The paper substrate showed a recovery time and quick reaction of 1.273 and 0.979 s, but the cotton substrate showed a rising time of 1.456 s, and time constants in the decay process are 0.686 and 1.323 s. Even at 0 V, the devices with paper and cotton substrates showed notable responsivities and detectivities even at 0 V, which are found to be 3.671 and 1.740 mA W^{-1}, and 3.092×10^{10} and 3.470×10^{10} Jones, respectively [64]. The platinum acetylide polymeric for organic SC was created by Mei et al., and it demonstrated the PCE of 1.1 to 1.4%, V_{oc} of about 0.5 V, and J_{sc} of about 7.2 mA cm^{-2} [78]. Han et al. fabricated the metallo-organic material for a SC with J_{sc} of 21.79 mA cm^{-2}, 0.719 of fill factor, and exceptionally robust and effective PCE. To produce a polymer perovskite composite (PCC), the polymer undergoes a stage of long-range ordering with the perovskite precursor. SCs made on $CH_3NH_3PbI_3$-PPC showed greater resistance to the environment. The device was mixed using a planar heterojunction and an Indium SnO_2/SnO_2 substrate, with a silver electrode. Additionally, they discovered during this experiment that using polymeric Lewis-based materials improved device stability, with only 64.3% degradation is recorded after 1008 h [79].

7 Summary and Outlook

Metallopolymer-based optoelectronic devices offer paramount applications in day-to-day life almost across several domains of science, including but not limited to sensing, communication, and energy. Several obstacles still hold back innovation as well as large-scale industrial implementation. These challenges need to be addressed to make these devices a practical reality. One of the major challenges is temperature sensitivity, as metallopolymer-based optoelectronic devices are often prone to thermal degradation, which affects their performance and reliability. Another challenge is the precise alignment of device components, which is crucial for optimal device performance. Additionally, integrating metallopolymer-based materials onto substrates can be challenging, as it requires specialized fabrication techniques. Although these obstacles are a major hurdle for the scientific community. But due to the paramount applicability of metallopolymer-based optoelectronic sensing devices, it holds huge potential for future improvement in present-day technology. Albeit, the futuristic implementation for strengthening and improving present-day technologies. Effective innovation would lead to low cost, enhanced performance, and large-scale industrial manufacturing and utilization. It's a well-known fact from recent breakthroughs that metallopolymers enhance optoelectronic properties. For instance, metallopolymers have been used in the development of OLEDs, and OPV devices, which have shown improved performance compared to traditional devices. In a nutshell, mechanisms and several types of optoelectronic devices are highlighted. Metallopolymer functional nanomaterials have reinforcing parameters that can be tailored to optimize the optoelectronics performance. By fine-tuning the composition and structure of these materials, researchers can achieve improved performance, increased durability, and lower costs. As a result, metallopolymer-based optoelectronic devices offer a huge potential for research and development (R&D) in industry and academics. Smart optoelectronic devices designed using metallopolymer nanoparticles have a bright future for communities in industry and academics. They offer several advantages over traditional devices, including lower costs, improved performance, and greater versatility. Thus, they have huge potential to revolutionize several domains of science, leading to more efficient and sustainable technologies for the future.

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Nanomaterials for Food-Agritech Sensing Application

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Abstract Global food security has been affected by increasing population, climatic changes, and usage of conventional agricultural techniques. These factors lead to demand for a shift in public policies and agricultural management towards a more resilient, efficient, and sustainable development model. The sustainable solution for these requires acceptance of new innovative approaches, particularly nanotechnology. Utilization of this technology and related products is increasing rapidly in agriculture in order to develop sustainable food-agritech systems. This approach facilitates the production of nanomaterials following atom by atom arrangement. Nanomaterials have the potential to facilitate the shift by encouraging mitigation, increasing productivity, and lowering contamination. To realize the potential of nanotechnology in producing inventive agrochemicals and novel delivery systems to improve crop productivity and quality, further investigation of nanotechnology applications in agriculture is required. This chapter compiles the most recent advancements in scientific research on smart nanoformulations and delivery systems that enhance plant nutrition and crop protection, nanomaterials as smart food packaging material, and nanosensors for plant health and quality of food and safety monitoring. Despite the fact that the use of nanotechnology in agriculture is still in its infancy, this new approach will gradually be discovered and will help in taking our society and agriculture to greater heights in the future. Therefore, it is extremely important to nurture this new technology in order to maintain sustainable food-agritech systems.

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1 Introduction

The agriculture sector faces many difficulties, including rapid climatic change, declining soil fertility, a lack of macro- and micronutrients, extreme utilization of pesticides and chemical fertilizers, and the existence of heavy metals in the soil. Also, the rise in the global population has, however, led to an increase in food demand. Providing food security for a world whose population is rapidly expanding is the biggest global challenge. The population is expected to increase to 9.7 bn. by 2050 and 11 bn. by 2100 and providing healthy nutrition will be a major challenge [1]. Farmers from all over the world will concentrate on utilizing modern advancements and technologies to improve crop yield via intensive and extensive agriculture. Precision farming and the usage of nano-modified stimulants will help the existing efforts even more. Basic elements of food security include agricultural productivity, soil enhancement, use of water securely, distribution of food in shops, and food quality. To preserve the standards of sustainable living of the nation and enhance food security, a newer technology that will enhance agricultural productivity while reducing food wastage is crucial. Advances in nanotechnology research may help to improve these aspects of food security and is shown in Fig. 1. For achieving sustainable agriculture, it is necessary to enhance the quantity and quality of agricultural products as well as the exploitation, management, and consumption of energy resources. It also involves protecting land, biodiversity, soil, and environmental health. These steps will improve social and economic conditions while improving health and developing a quick-response, versatile system that can adapt to climate change [2].

The multidisciplinary field of nanotechnology research has demonstrated progress in the areas of medical, biotechnology, environmental science and food technology, engineering, and agriculture. It entails the molecular-scale manipulation of matter to create structures known as "nanoparticles" (NPs) which are less than 100 nm (in size) in at least one dimension. Because of the high surface-to-volume ratio and small size, NPs have unique characteristics that distinguish them apart from their bulk counterparts. Numerous research have examined the cytotoxic effect of NPs on cancerous cells for use in medical sciences. Like this, various research on the use of NPs as antibacterial agents have been carried out [3].

One of the potential fields in which new products can be produced for uses in agriculture, water, food, energy, medicine, and electronics is nanotechnology. It is an emerging and constantly expanding area with novel and exclusive applicability in agricultural and food research. The basic parameters for selecting nanomaterials in food-agritech applications are particle size, molecular weight, charge, composition, and solubility. The usage of nanomaterials in agriculture is developing in a few areas, including reducing the amount of chemicals used in pest control and fertilization and minimizing nutrient losses. Wang et al. [4] observed an increase in the chlorophyll

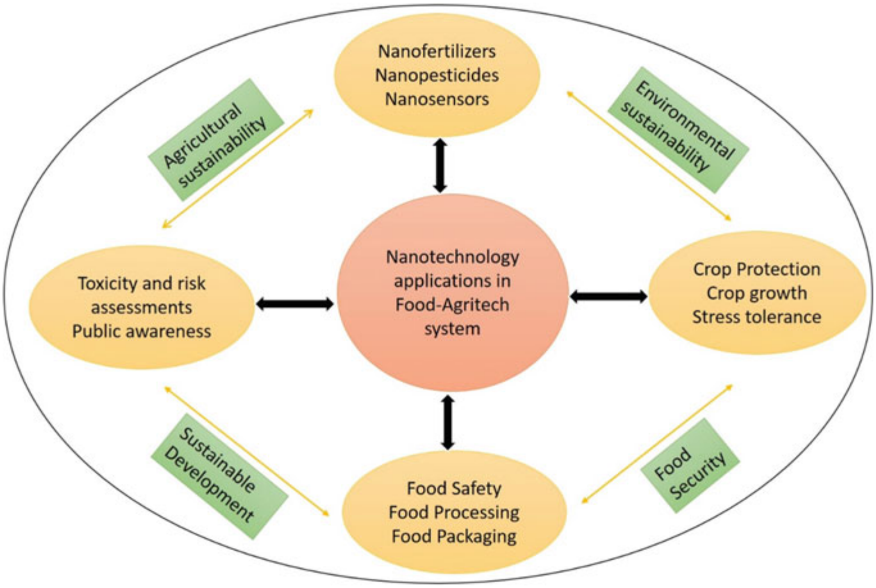

Fig. 1 Applications of nanotechnology in food-agritech system

content and photosynthesis of the coffee using Zn/B nanofertilizer prepared by ionic gelation. This nanofertilizer also promotes growth of the coffee plants by enhancing the uptake of zinc, phosphorus, and nitrogen. Tarafdar et al. [5] have also observed 37.7% improvement in the grain yield at crop maturity by application of zinc nanofertilizer. Silver, copper, carbon, silicon, and magnesium-based NPs have been used as nanopesticides in order to increase and improve agricultural yield and efficiency by shielding plants from harmful elements such as insects and plant diseases [1].

In order to reduce environmental effects while maintaining plant disease resistance and agricultural productivity, nanofertilizers and nanopesticides release active chemicals in a controlled and targeted manner. Nanosensor devices can be used to detect either plant stress or food safety and quality. In a similar way, they assist in the preparation and packaging of food. Food nanotechnology involves using nanocarrier techniques to increase the bioactive substances in order to change the biological accessibility and barrier against various chemical or environmental changes. It induces food products with novel nutritional, sensory, and physicochemical properties such as texture, appearance, flavor, and stability. The food industry is gaining from nanotechnology as novel food packaging materials with enhanced mechanical, and antibacterial qualities. Other benefits of the technology included the ability to encapsulate food additives or modifiers, monitor diet status in terms of transportation and storage, and use nanotechnology-based sensors for sensing of traces.

Applications of nanotechnology have increased the demand for using NPs in food biotechnology, food packaging, food processing industry, functional food production, pathogen sensing in food, food safety, and extending the life span of food and food products. Nanomaterials are very effective at improving food security to support the growth of food production sector. Depositing food processing machinery, nanofabricated sieves, filters, and membranes, as well as nanocomposite-based and nanosized adsorbents, is another use for the provision of assistance in food processing. The inclusion of NPs in food packaging is intended to reduce the need for valuable raw ingredients and waste production while also altering the resistance experienced during material packaging [6].

Generally, nanotechnology offers the most promising potential for the advancement and improvement of various products. The focus of this chapter is to explain the fundamentals of nanotechnology, its applicability in agriculture, food processing technology and packaging, and its role in assisting efforts to ensure food security, as well as the difficulties in implementing this technology in the food-agritech system.

2 Basics of Nanotechnology

Richard Feynman, the inventor of “Nanotechnology” and a Nobel Laureate in Physics, introduced the concept at the annual meeting of the American Physical Society (in 1959) and used the phrase “There is plenty of room at the bottom” to describe the virtually limitless possibilities for controlling and manipulating things on a nanoscale. Nanotechnology is the synthesis, characterization, and utilization of extremely small particles known as “nanoparticles” (NPs), which have at least one of the dimensions in the range of 1–100 nm. One nanometer is equal to one billionth (10^{-9}) of a meter, indicating that technology can be used at this scale. The unique properties of NPs, such as their size in nanoscale i.e., 1–100 nm range, high surface-to-volume ratio, reactivity, quantum size effects, physical strength, electrical, optical, and magnetic properties, are what give them such a large range of applications in the fields of agriculture, medicine, cosmetics, industries, etc. As the size reduces, the surface-to-volume ratio increases significantly, making NPs extremely reactive with novel and distinct features (such as quantum confinement) that are different from their macroscopic bulk counterparts and atomic or molecular structures. They can take on the forms of nanotubes, nanoparticles, nanofibers, fullerenes, nanosheets, and nanowhiskers [2].

NPs can be synthesized using two distinct approaches: one is a top-down approach and the other is a bottom-up approach. The top-down techniques, including milling, ion implantation, and mechanical grinding, are often carried out by breaking down and slicing bulk forms into NPs. For instance, dry milling process is used to obtain grain flour with a smaller particle size and a higher capacity to hold water. If the size is reduced, the top-down strategy can improve the antioxidant qualities of green tea. An article reports that green tea powder with a particle size of 1000 nm has improved nutritional absorption, which increases the activity of an oxygen-eliminating enzyme, leading to increased antioxidant activity. Contrarily, biology-derived ideas such as self-assembly and self-organization have influenced the development of bottom-up food nanotechnology. Casein micelles, globular proteins, starches, and protein aggregates are examples of self-assembly structures that result in stable entities [7]. By striking a balance between the various non-covalent forces, self-organization on the nanoscale (scale) can be accomplished. The bottom-up techniques, involve the sol-gel process, green synthesis, pyrolysis, and electrolysis, which work by assembling smaller atoms or molecules into larger NPs.

3 Applications of Nanoparticles in Agriculture Sector

The increasing demand for food with a rapidly growing global population has pertinent issues in the field of agriculture. New techniques and strategies are developing continuously to deal with these demands. With the use of nanoparticles (NPs), modern agriculture is evolving into precision agriculture in order to maximize yield from the resources at hand. In the agriculture sector, the main focus of NPs is to decrease nutrient losses, increase plant growth and crop yield [1], and find many applications in different sectors which are described below.

3.1 NPs as Nanofertilizers

Fertilizers are an essential part of agriculture as they boost crop productivity. But the growth of crops is at the cost of diminishing soil fertility as most fertilizers disturb the soil-mineral balance. Fertilizers can be applied through soil irrigation, root treatment, and foliar method that can cause damage to the ecosystem. To maintain the desired need of food, chemical fertilizers are used abundantly which ultimately causes soil deterioration, environmental, and water pollution.

To achieve food security, environmental sustainability, and agricultural sustainability, targeted delivery of these nano-agrochemicals either through foliar or soil application protects crops from a variety of pests and improves nutrient utilization and uptake efficiency for improving crop growth and yield.

Therefore, Nanofertilizers are being explored as an alternative to chemical fertilizers for relevant agri-technology to assure long-term favorable agriculture strategies for safeguarding security globally as shown in Fig. 2. Through their slow nutrient release and improved nutrient use efficiency, nanofertilizers might have a beneficial effect. Nanofertilizers are nutrients encapsulated with different types of NPs that offer slow release of nutrients for necessary nutrient requirements of plants. Nutrients are bound to nano-dimensional adsorbents, like nanotubes or nanoporous materials, thin layer of polymer, etc. Due to enhanced surface-mass ratio of NPs, there is also an increase in absorption of nutrients by roots. Nanofertilizers can also be applied through soil or foliage method depending on the physical and chemical properties. Nanofertilizers are economically cheaper and are required in lesser amounts as compared to chemical fertilizers.

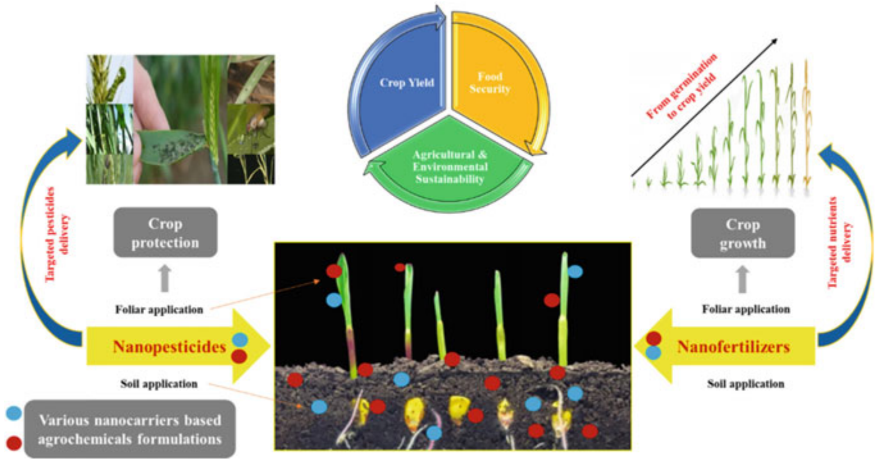

Fig. 2 Schematic illustration showing how nanopesticides and nanofertilizers are used in modern agriculture [2]. Open Access (2021) MDPI

Nanofertilizers are synthesized to match the crop nutrient requirement as different crops have different nutrient necessities. Silicone-based nanofertilizers help in mitigation of salinity stress which could have happened because of high surface ratio of the NPs. Similar to this, nanosilica-coated fertilizer creates a binary coating on microbial cell walls that enhances plant disease resistance and promotes root and seed development [8]. Zeolite based nanofertilizers are capable of slow delivery of encapsulated nutrients so that the nutrients are available to plants throughout the growing season. The application of different NPs in fertilizers through different means (such as foliar spray, seed coating, and soil irrigation) and their responses are given in Table 1.

3.2 NPs in Seed Germination

Germination of seed is the first step and is considered as the most crucial stage of the plant life cycle. NPs have a great potential in promoting seed germination of plants. NPs help in rapid growth of seeds, speedy development of the leaves, and growth of the roots that in turn favor the absorption of nutrients and their translocation via transpiration. During seed germination, NPs initially enter the seed coat which usually contains sclerenchyma and it can act as a barrier for the NPs due to their physical-chemical integrity. The process of seed germination takes place in three phases as described in Fig. 3 [23].

Phase I of seed germination begins with imbibition, where water exchanges rapidly. The basic metabolism of seed, including transcription, protein synthesis, and mitochondrial activity, is triggered by the quick intake of water. Phase II (also

Table 1 Application of NPs in fertilizers and their responses

NPs in nanofertilizers	Crop species	Concentration	Mode of application	Response	References
ZnO	Cherry tomato	4.5–4.8 mg Zn/kg^{-1} in the acidic soil	Soil grown	Increase in B concentration and decrease in Cu concentration	[9]
ZnO	Lettuce	10 mg Zn/kg	Root	Increase biomass and photosynthetic rate	[10]
Cu	Alfalfa (medicago sativa)	80 mg Cu/kg		Better agronomical responses than ionic Cu	[11]
Potassium	Wheat	20 ppm, 40 ppm, 60 ppm	Spray	Enhanced crop yield, protein content, and photosynthetic pigments	[12]
Ag	Fenugreek plant	40 mg/L Ag NP	Foliar treatment	Improvement in growth, biochemical parameters, and yield of fenugreek	[13]
Fe	Black-eyed pea	0.5 g L^{-1}	Foliar application	Efficient photosynthesis	[14]
CeO_2	Cabbage		Soil	Improvement in growth parameters	[15]
CuO	Lettuce	31 mg Cu/kg	Soil	Improvement in nutrient absorption	[16]
Nano-sulfur	Rice	200 mg/kg	Soil	Increase in rice seedling biomass plant seed production	[17]
Copper hydroxide	Soybean	0.36, 1.8, and 9 mg	Foliar application	Activation of important biological processes	[18]
TiO_2	Coriander	50, 100, 200, and 400 mg/L	Hydroponics	Improved the nutritional quality of coriander	[19]
Si	Rice	5 mM	Foliar application	Decrease in metal toxicity in grains	[20]

(continued)

Table 1 (continued)

NPs in nanofertilizers	Crop species	Concentration	Mode of application	Response	References
Se	Rice	40 mg L^{-1} Se with 0.1% Tween 80	Foliar application	Reduced toxicity and reactive oxygen species accumulation and improved nutrient balance	[21]
Fe	Wheat	0, 25, 50 and 100 mg/kg	Soil application	Improved shoot dry weight and photosynthesis while oxidative stress decreased	[22]

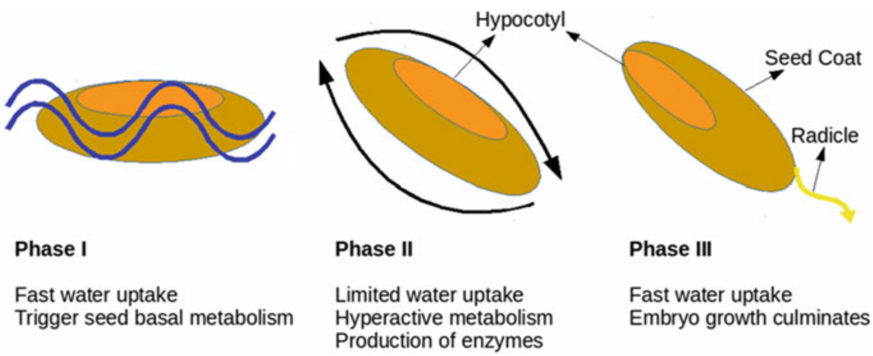

Fig. 3 Different phases of seed germination

known as activation or lag phase), limits the uptake of water which makes metabolism hyperactive with the production of enzymes. Enzymes help in the development of an embryo, which includes phytase, endoxylanase, and amylases. In phase III, the seeds again exhibit fast uptake of water, and the growth of the embryo results in radicle protrusion [23].

Different NPs have different effects on seed germination. Metal-containing NPs have both positive as well as negative impacts on the process of seed germination. Metal oxide NPs (TiO_2 and ZnO) penetrate the seed coat where it provokes the embryo to differentiate, resulting in the emergence of a radicle from the new progeny. After interaction with the NPs, the growing tissues of the root apex travel via symplastic routes to the vascular cylinder before being translocated to other developing plant parts [24]. TiO_2 by improved water adsorption but NPs show no change in the germination process [25]. However, for onion seeds increase in antioxidant enzymes (peroxidase, catalase, and superoxide dismutase) and hydrolytic enzymes (protease and amylase) activity is observed using TiO_2 NPs by Laware et al. [26]. CuO NPs have a negative effect on the germination process and transpiration rate in spring barley that also inhibits plant growth. The negative effect of CuO NPs in the germination of cucumber seeds is also reported at 200 and 600 mg/L concentrations by Moon et al. [27]. However, CuO NPs have not shown any toxic effects on chickpea, soybean, rice, and maize even at higher concentrations [28]. Ag NPs help in the germination of watermelon and zucchini seeds and root elongation at particular concentrations. Mahakham et al. [29] have observed that nanopriming rice seeds with Ag NPs enhanced antioxidant enzyme activity and α-amylase that promotes seedling growth which in turn enhanced seed germination. Zhang et al. [30] observed enhanced seedling growth and seed germination in graphene-treated tomato seeds even at low concentrations. Graphene enhances the germination process as it can easily penetrate the seed coat, facilitating higher water uptake which speeds up the germination process. Almutairi and Alharbi [31] reported a faster germination process and root elongation in watermelon and zucchini seeds primed with Ag NPs even at low concentrations (0.5–2.0 g L^{-1}). Thus, different plant species respond in their own way to NPs. These variations are due to the lipid content present on the seed coat, as the constituents of the seed coat can affect NPs aggregation on the surface of the seed.

3.3 NPs in Abiotic Stress Management of Plants

The growth of plants is affected adversely by abiotic stresses like extreme temperature conditions (heat and cold), water logging, and ion toxicity due to salinity and heavy metals. This abiotic stress induced by environmental conditions results in developing various defense mechanisms in plants that are encountered at various growth stages. This stress leads to oxidative damage in plants by producing cytosolic accumulation of toxic ions and reactive oxygen species (ROS) that restrict plant growth and productivity. In addition to being toxic and harmful, ROS can also play a vital role in intracellular and intercellular signaling. Non-enzymatic antioxidants that support the antioxidant defense systems and are linked to stress tolerance include glutathione, anthocyanin, ascorbates, and thiols.

Now-a-days NPs are being explored to decrease the negative effects of abiotic stresses in plants. Due to high aspect ratio of NPs, these can easily cross the barrier of cell wall and plasma membrane. Their further movement depends on the osmotic pressure and capillary forces. The scope and role of NPs as a useful tool to diminish the negative impacts of various abiotic stresses are described below.

3.3.1 Heavy Metal Stress

As industrialization is growing gradually, the waste material of these is disposed directly to the agricultural lands and water resources. The waste material of industry and fossil fuel combustion contains toxic metals and contaminates both soil and water. These toxic metals are very hard to degrade and easily transferable from the environment to humans [24]. Plants uptake these metals through soil and water by active or passive transport processes. These metals exist in an oxidative state due to which they can transport to the plasma membrane and affect the cellular and molecular level. Due to high reactivity of these metals, they affect enzyme activity and protein denaturation, and destroy the plasma membrane. Heavy metals can also accumulate in the root tissues of some plants, which inhibits the flow to the aerial system and affects the growth and development of the plant. Cadmium, nickel, chromium, lead, copper, and mercury are the main toxic heavy metals for plants. Heavy metals possess different effects on the plant species depending on their physical and chemical properties such as accumulation of cadmium results in the production of ROS, oxidative damage to cells, inhibition of photosynthesis and metabolic activity, decrease in regulation, imbalance water uptake and decrease nutrient absorption in plants [32–35]. Lead and copper heavy metals cause water uptake imbalance in plants whereas zinc and chromium inhibit the metabolic activity of enzymes. Copper, mercury, and nickel heavy metals cause oxidative damage and ROS generation. All these heavy metals easily enter the human body via the food chain and lead to serious health issues like diabetes, cancer, cardiovascular disease, hypertension, etc.

NPs can decrease the accretion of the above toxic metals as they can easily bind with these metal ions and trigger plant defense system by accumulating necessary ions like K^+ or Ca^{2+} thereby decreasing their negative effects. Different type of NPs has different effect on the toxicity of heavy metals. Carbon Quantum dots restrict the entry of lead and copper toxic ions via roots and reduce their availability to plants. Carbon dots are also efficient for reduction of cadmium toxicity in wheat roots and leaves as they can easily absorb cadmium ions [36]. Application of Fe NPs, significantly improves wheat biomass and photosynthesis under cadmium stress. Konate et al. [37] observed that Fe_3O_4 NPs diminish heavy metal uptake by reducing oxidative stress induced by cadmium and lead, thus mitigating their toxicity in wheat seedlings. Manzoor et al. [38] synthesized FeO NPs and observed that application of FeO NPs in wheat plants significantly increased the necessary mineral nutrients like N, P, and K^+ in cadmium polluted soil and reduced plant uptake of cadmium due to much absorption of cadmium on large surface of NPs. ZnO NPs also increased wheat growth and yield while reducing Cadmium uptake in grains [39]. In addition to these, there are many NPs like TiO_2, Si, and CeO_2 that help in the reduction of toxic effects of heavy metals and improvement in plant growth, some of these are illustrated in Table 2.

3.3.2 Drought Stress

The optimal amount of water is necessary for the growth of plants. Water deficiencies in the plants lead to drought stress which inhibits seed germination, photosynthesis, flowering, and fruiting by ROS generation thus hindering plant growth and reducing crop production. Global climate change, rainfall anomalies, and shifts in monsoon patterns are the main causes of drought stress. Different approaches and strategies are

Table 2 Effect of NPs in increasing the tolerance against heavy metals for different plants

Nanoparticles	Plant species	Heavy metal	Effect	References
TiO_2	Rice	Cd	Reduce Cd uptake in roots and leaves, Photosynthetic rate and chlorophyll content increases	[32]
TiO_2	Wheat	Cd	Enhanced plant height, spikes photosynthesis, and grain yield	[33]
ZnO	Maize	Cd	NPs improved chlorophyll, root, and shoot dry biomass, while reducing MDA, H_2O_2, and Cd concentration	[34]
ZnO	Wheat	Cd	Decrease in oxidative stress and enhanced chlorophyll content and antioxidant enzyme activities	[35]
Si	Wheat	Cd	Improved biomass of shoots, roots, spikes, and grains and decreased oxidative stress	[40]
Si	Rice	As	Increase in activity of antioxidant enzymes and enhanced defense capacity	[24]
SiO_2	Pea	Cr	Increase in photosynthesis, plant growth, and mineral nutrients in plants while decreased Cr in plants	[41]
Silica NPs	Wheat (*Triticum aestivum*)	Cd	Improved the growth and development of the plant	[42]
Si NPs	Rice	Cd	Increased the photosynthetic capacity	[21]

used to lessen the adverse impacts of drought stress. The negative impacts of drought stress can be mitigated by the application of NPs, as these are capable of adjusting osmotic pressure and improving the ability of tissues to absorb and retain water in plants. Application of Si NPs dramatically enhances seedling growth, defense response, and other physiological parameters of plants under drought stress conditions. Alsaeedi et al. [43] observed that Si NPs improved growth and productivity of cucumber by increasing the nutrient uptake in root, stem, and leaf by regulating water loss by transpiration. According to Adrees et al. [22] soil treatment by Fe NPs boosted the photosynthesis and reduced the oxidative stress in wheat by mitigating drought stress thereby increasing the yield. Metal NPs activates antioxidant defense mechanism and improves plant's tolerance to various abiotic stresses. Zn NPs also help in root development and drought tolerance in plants. Taran et al. [44] have reported that Zn NPs and Cu NPs significantly improve the tolerance against drought stress in wheat plants as these NPs enhance antioxidant enzymes against ROS and stabilize photosynthetic pigments.

3.3.3 Salinity Stress

Salinity stress is the non-biological stress that has adversely affected approximately 20% of cultivated land across the world and this amount is even growing. Salinity stress is caused by the accumulation of ions (Na^+ and Cl^-) in plant cells that leads to morphological, physiological, and molecular changes in plant cells. Due to salinity stress soil osmotic ability decreases, ionic toxicity increases, and nutrient levels are disturbed. Furthermore, salinity stress also causes oxidative stress, hormonal imbalance, and photosynthesis disturbance. These negative impacts disturb plant growth and decrease plant yield. Plants can develop a defense system for their protection from the harmful effects of salinity stress.

NPs improve the ability of plants to tolerate salinity in a variety of ways as shown in Fig. 4. By boosting the number of photosynthetic pigments in plants under salinity stress, the majority of NPs were found to promote photosynthesis [45]. Iron oxide NPs facilitate photosynthetic pigments and enhance tolerance to salinity stress in wheat [38]. Perez-Labrada et al. [46] reported that, foliar spraying of Cu NPs improved the development of tomato plants and the Na^+/K^+ ratio under salinity stress. Khan et al. [47] described that when pearl millet primed with Ag NPs (10, 20, and 30 mM) under salinity stress (0, 120, and 150 mM NaCl), growth increases significantly which was ascribed to an increase in antioxidant enzymes and decrease in sodium to potassium ratio.

The usage of NPs regulates salinity tolerance in plants by balancing ion homeostasis, regulating the biosynthesis of osmolytes and phytohormones, antioxidant defense system, and improvement of photosynthesis. NPs enter plant tissue when

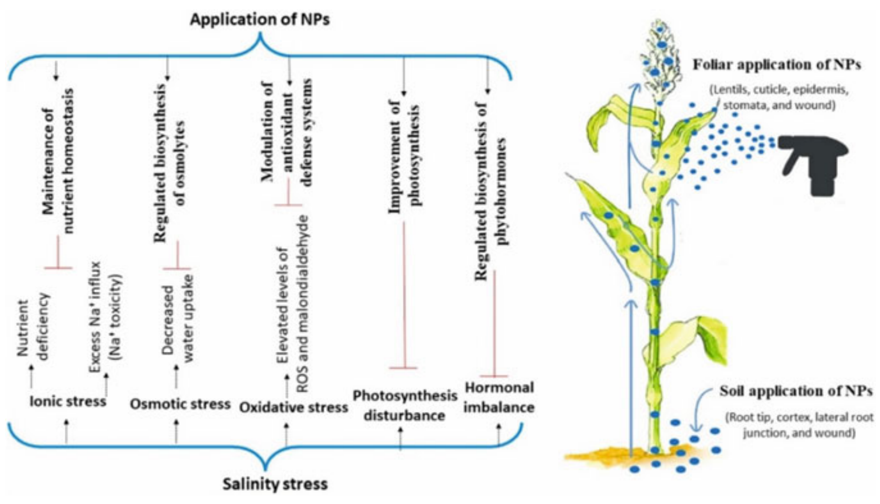

Fig. 4 Several mechanisms of plant salinity stress resistance generated by NPs [45]. Open Access (2021) Elsevier

exposed to plants through the root-leaf junction, leaves, and abrasion. They subsequently penetrate the cell wall and cell membrane of the root epidermis. Thereafter, they engage in cellular and subcellular interactions with the plants, resulting in altering the molecular states and raising the osmotic potential of the plants.

Si NPs found to improve oxidative stress tolerance in sweet orange under salinity stress conditions. Si NPs promote better growth and yield as these can affect light harvesting complexes and alter synthase complex genes such as photosynthetic genes, biosynthesis genes, and stress genes. It has also been reported that Si NPs have positive effects on seed germination, seedling, chlorophyll content, and antioxidant enzyme content in tomato, basil, lentil, and pumpkin plants [48]. Hernandez et al. [49] reported the impact of Cu NPs on tomatoes under salinity stress and observed a decrease in ionic and oxidative stresses. Cu NPs have effectively increased tolerance to salinity stress by activating antioxidant defense mechanism. Gold NPs also found to improve plant defense system and increase tolerance of salinity stress in wheat [50]. Yasmin et al. [51] have reported that ZnO NPs promote plant growth under salinity stress by improving the antioxidant enzyme activities in Safflower. According to Manzoor et al. [38], FeO NPs improved the growth, chlorophyll levels, and antioxidant enzymes in wheat plants, which reduced the effects of salt stress.

3.3.4 Heat Stress

Temperature is one of the most harmful among the ever-changing environmental conditions, which is always rising as a result of global warming. When the temperature exceeds the ideal range, the physiological and molecular mechanisms of plants get disturbed. Excessive temperature causes heat stress, which interferes with photosynthesis and inhibits plant growth. According to several research studies, NPs could be used to increase the ability of crop plants to withstand heat stress. Thakur et al. [52] studied the effect of ZnO and TiO_2 NPs seedling of wheat under high-temperature conditions and found that TiO_2 NPs slightly outperformed ZnO NPs in terms of increased seedling performance, while ZnO NPs had a stronger antioxidant defense response. By opening the stomata, TiO_2 NPs considerably lowered the heat stress and enhanced plant growth and photosynthesis efficiency in tomato plants [53]. TiO_2 NPs also promoted the growth of plant and antioxidant activity in cold conditions.

3.4 NPs as Nanopesticides

In the agronomic field, it is very well known that pests and insects are the main destroyers that have a negative impact on the development and yield of crops. Nowadays, NPs are being tested as pesticides to prevent harmful pests from attacking various crops. Nanopesticides have special properties such as enhanced specificity, solubility, permeability, and stability that can enhance agricultural productivity and ensure food security and sustainability (shown in Fig. 2). Metal NPs exhibit good antipathogenic, antimicrobial, antibacterial, and antifungal activities due to their electrostatic interaction with the cell membranes of bacteria and their accumulation in the cytoplasm [54]. These NPs also inhibit the growth of a number of pathogens. The ability of Ag NPs to prevent microbial development by preventing the germination of their spores makes them a potent nanopesticide [14]. The antimicrobial activity of Ag NPs has been employed to combat a variety of plant pathogenic bacteria. Si and Zn NPs treatments at 100 mg L^{-1} dramatically increase the catalase and peroxidase activity i.e., 40 and 65% and 99 and 208%, respectively in *N. benthamiana* [55]. Thus, nano-encapsulated pesticide is very effective because of its slow and sustained release that allows appropriate chemical absorption into the plants and has a persistent and long-lasting effect.

3.5 Nanosensors in Plant Protection

The hybridization of biosensors with different NPs offers several conjoining and multifunctional strategies to enhance the sensitivity for detection. Nanoscale element devices such as nanosensors are designed to detect a specific biological component, molecule, or environmental condition. The three fundamental parts of a typical nanosensor device operation are (i) sample preparation, (ii) recognition, and (iii) signal transduction which are described in Fig. 5. Nanosensors are utilized for the measurement of nitrogen uptake, soil parameters (nutrients and pH, residual pesticides in soil and crop, and soil humidity), and the detection of pathogens [56]. During the growing season, cultivated fields are continuously monitored in real time using a nanosensor-based global positioning system (GPS). They use wireless signals located all across the cultivated fields to monitor the controlled release mechanism using nanoscale carriers. In addition to avoid excessive usage of agricultural chemicals, the controlled release mechanisms via nanoscale carriers monitored by nanosensors also aid in minimizing pesticide and fertilizer inputs during cultivations, increasing productivity and lowering wastage. Thus, development of nanosensors is required for the optimization of crop growth and environmental systems.

Agroecosystem sample preparation is highly difficult because of contaminants and interferences. Specific molecules, functional groups of molecules, or organisms that the sensors can target are present in the sample. The analytes are the targeted molecules or organisms. The analytes present in the sample are recognized by particular molecules or elements. These recognition molecules, which include antibodies, aptamers, chemical legends, enzymes, etc., have strong affinities, specificities, and selective properties to their analytes that enable their quantification to acceptable levels. These simple devices have been divided into various categories by specific signal transduction techniques, including optical, electrochemical, piezoelectric, pyroelectric, electronic, and gravimetric biosensors. They transform recognition events into signals that are analyzed to generate data (as shown in Fig. 5).

ICTS sensors based on Au NPs have been found to have limited detection sensitivity, due to the production of considerably weaker color density, which restricts

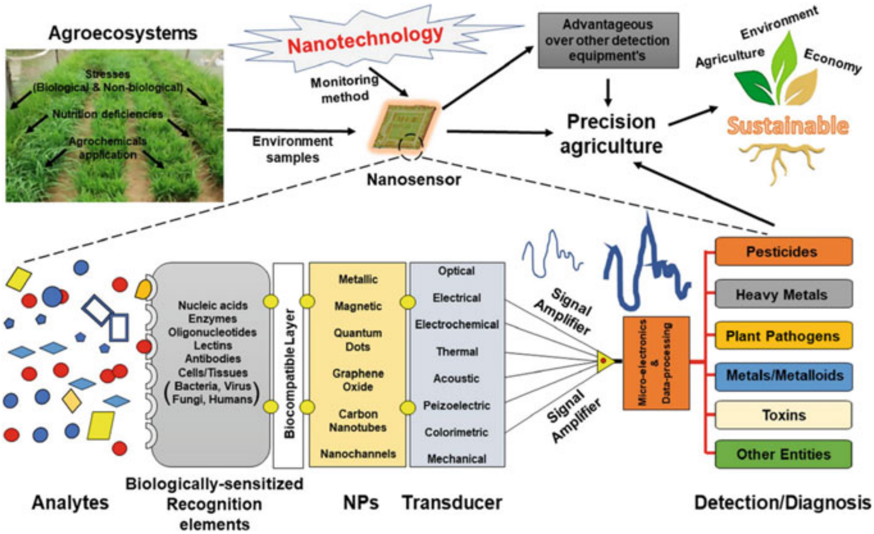

Fig. 5 A simplified illustration showing how nanosensors are used to monitor agroecosystems [56]. Open Access (2021) Springer

their application [57]. However, a number of suggested amplification techniques can increase their sensitivity. Every time a pathogen infects a plant, it creates distinctive volatile signatures (also known as plant volatiles), and the identification of these signature molecules can help in confirming the presence of a pathogen infection in plants. Using SWCNT sensors in the specific region of the leaf, which will provide fluorescence intensity, it is also possible to track short-lived signaling molecules including glucose, nitroaromatics, and ROS [58]. The humidity sensing performance of $CuWO_4$ NPs was tested by Patil et al. [59] and the sensitivity of the device was found to be ∼767 at 97% relative humidity level which demonstrated that this humidity sensor device has the potential to be used as a portable device for controlled humidity detection.

4 NPs in Food Technology

A more sustainable and resilient food production, processing, and storage is considerably improved by the use of nanosensors and other nanotools in conjunction with computer-based control systems.

The field of food nanotechnology is gaining attention and offers a variety of fresh opportunities for the food industry. Two important applications related to nanotechnology in the field of food engineering are food processing and food packaging and are shown in Fig. 6.

Fig. 6 Illustration of application of nanosensors in food processing and packaging [2]. Open Access (2021) MDPI

4.1 NPs in Food Processing

The largest food firms on a global scale are looking into a number of ways to change the quality, value, nutritional, and safety properties of food. In order to increase productivity, quality, and market price, the food industry needs newer technologies. Numerous applications of nanotechnology are being developed for the manufacturing and processing of food, including nanosensors, food additives based on nanotechnology, nanoencapsulation, nanopacking, smart distribution systems based on NPs, as well as medications and health care [6]. In particular, flavor encapsulation or odor enhancement, texture modification or value enhancement, and novel gelation or viscosity raising agents are driving the growth of industrial food processing using nanotechnology. Food nanotechnology places a significant focus on the creation of nanometer-scale structures, characterized by special qualities that can be applied to a variety of applications, such as food characterization tools, delivery systems, microfluidic instruments, surfaces for food interaction with distinctive superficial properties, sensor technology, and nanocomposite coatings, among various others. Nanomaterials are used in the food processing industry as anti-caking agents, food additives, antimicrobial agents, and transporters that deliver nutrients effectively, adding fillers to the packaging material to boost its mechanical strength and stability. Food nanosensors are also used to improve the security and value assessment of the food [60].

Nanofiltration, nanoencapsulation, nanoscale enzyme reactors, heat and mass transmission, and nanofabrication are all multipurpose applications of nanotechnology in food processing [6]. Pharmaceuticals can be purified more effectively by nanofiltration, Additionally, it is used to modify the quality of dairy products by removing salt from lactose, as well as drinking water purification. Heat resistance of the package was improved through heat and mass transfer nanofabrication. Nanoscale enzyme reactors are used in food processing to change food mechanisms for improved flavor, dietary value, and a variety of health benefits. Application of the nanoencapsulation procedure enhances food items. This method is frequently used to preserve food, increase flavor, and provide cooking balance. A further demonstration of resemblance to other components of the system, nanoencapsulation conceals tastes and odors, manages how food interacts with active components, controls the release of dynamic agents, safeguards accessibility at a specific time with a specific rate, and protects against heat, chemical, biological or moisture interference during processing, storage, and application [61].

4.2 NPs in Food Packaging

Food storage with preserved nutritional properties is made possible by food packaging, which is a crucial component of the food industry. Food packaging not only keeps the food from spoiling but also shields the delicate bioactive chemicals from damaging physical and environmental factors. There is a lot of research being done on nanotechnology to enhance food packaging. Functional NPs have been discovered to strengthen barrier qualities, durability, thermal stability, and strength of packaging materials, which help extend food product shelf life. In food packaging, silver (Ag), ZnO, Chitosan, carbon nanotubes, nanocellulose, nanostarch, and TiO_2 are very valuable materials. Li et al. [62] synthesized antibacterial chitosan-gelatin microcapsules, modified with Ag NPs, and blended them into the biopolymer polylactic acid (PLA), to form films. In this study, it was found that the synthesized films showed antibacterial properties against *S. aureus* and *E. coli*. The results of using the antibacterial PLA films to preserve grass carp fillets to increase their shelf life proved that they had an antibacterial effect on food and hence can be used as sustainable and functional food packaging material.

Better physical and mechanical packaging, active packaging with antibacterial, antioxidant, and UV absorption capabilities, and smart packaging with monitored/controlled food conditions are all made possible by nanotechnology. Amini et al. [63] developed an eco-friendly and effective method for making hydrophilic cellulose fibers compatible with hydrophobic polycaprolactone (PCL) by using an ionic liquid (as a nanowelding agent) in the presence of zinc oxide (ZnO) NPs. Transparent bio-based nanocomposite films were synthesized and these films demonstrated acceptable UV-light barrier qualities and antioxidant activity, indicating that they have potential for usage in the packing of food. Because they are transparent, bio-based, and have excellent water vapor and oxygen barrier qualities, nanocomposite films can be used in cellulose-based food packaging. Liang et al. [64] synthesized nanocomposite film by combining natural pectin film with natural melanin

NPs and with near-infrared (NIR) triggering. The findings demonstrate that synthesized films have highly effective short-term bactericidal efficacy against foodborne pathogenic bacteria, including thermotolerant *Listeria monocytogenes.* Additionally, this film displayed better antibacterial ability, thermal stability, barrier, and mechanical properties as compared to neat pectin film and will effectively promote edible nano-antibacterial packaging.

One of the most effective applications of nanotechnology is the use of nanosensors to keep track of the internal and external conditions of fresh and processed food products. Numerous indicators, including pH indicators, time-temperature indicators, and leak indicators, have been created to monitor the food quality since some foods are extremely perishable and deteriorate when storage conditions change [65].

5 Challenges and Future Perspectives

Innovations based on nanotechnology are expected to change the existing traditional agricultural system to a highly effective, sustainable, and resilient agricultural system. But, it should be noted that nanotechnology-based techniques are still in their early stages of development, and more work is required to create environmentally safe, economically viable, more stable, effective, and multifunctional nanomaterials. The main concern with nanotechnology is the small and compact size of NPs with larger surface areas that can easily penetrate cells to reach distant places within the body and can potentially cause toxicity [6] as from the toxicity perspective, the two most significant features of NPs are size and concentration. As a result, extensive trials must be conducted in order to advance and build futuristic research based on identified knowledge deficits. In this scenario, we suggest the following fundamental features:

- The majority of nanomaterial applications take place in controlled laboratory conditions, where nutrient behavior from coated materials to the target could differ from that under natural circumstances. To gain a deeper understanding of the release behavior of engineered nanomaterial large-scale in-field experiments based on research data derived from strictly monitored laboratory conditions are strongly advised.
- To determine the lowest concentration dose of the NP that is non-toxic and can be applied in the field using the concentration-dependent study in the natural soil system.
- To prevent its misuse at the toxic level, it is essential to harmonize the regulatory frameworks for nanosafety, while emphasizing safety-by-design synthesis techniques.
- The primary goal of environmentally oriented nanosafety research must be to examine the unintentional environmental releases of NPs that occur during the production, use, and disposal of nanoformulated agriculture nanoproducts.

- The dissemination of new knowledge and technological advancements to farmers is frequently lacking in many nations, particularly emerging nations, which hinders their potential to increase production and income and this should be prioritized.

6 Conclusion

Nanotechnology is a relatively new technology which is increasing rapidly in various domains that are relevant to human activities and advantages on a global scale. Due to their increased surface area, small size, and highly catalytic nature, NPs, and nanostructures have been demonstrated in several studies to improve a variety of attributes. In the agricultural sector, particularly, nanotechnology is essential for establishing food security. With great economic value, security, and safety, it can increase crop yield by effectively controlling pests, microorganisms, and weeds. Additionally, it is essential for food modification, food processing, sensing, stability, reducing food losses, extending shelf life, and providing food safety. Ag, Au, TiO_2, Zn, ZnO, MgO, and SiO_2 NPs, which are frequently used in the food processing industry, may also be harmful for health because they can easily penetrate cells and have the potential for adverse reactions in a variety of human organs, animal organs, and plant parts. By controlling the parameters (size and concentration), the toxicity level of the plants can be controlled. Future studies could reduce these risks from NPs or composites by employing greener synthesis techniques and looking for quick, inexpensive methods for degrading and removing existing nanomaterial from potential attack areas.

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