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REVIEW ARTICLE

Electrospun Polyaniline/Polyacrylonitrile Nanofibers for Room Temperature Gas Sensing: A Review

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ABSTRACT

Gas sensors utilizing conducting polymers such as polyaniline (PANI) and polyacrylonitrile (PAN) as active layers are reviewed. This overview delves into the sensing mechanisms, sensor configurations, and the various factors impacting sensor performance. Specifically, a PANI/PAN nanofiber, synthesized through electrospinning and *in situ* chemical polymerization, is examined for its response to different concentrations of volatile organic compounds such as methanol and acetone at ambient temperature. Notably, the sensitivity of the PANI/PAN sensor is found to correlate positively with increasing concentrations of methanol and acetone.

Key words: Electrospinning, Gas sensing, Nanofibers, Polyacrylonitrile.

1. INTRODUCTION

Conducting polymer nanocomposites (CPNCs) show great promise for sensor devices, offering a unique blend of properties including design flexibility, heightened sensitivity, and the ability to operate at low temperatures. By incorporating nanomaterials into conducting polymers, CPNCs can be engineered to detect a wide range of analytes with high sensitivity, making them valuable for various sensing applications such as environmental monitoring and healthcare diagnostics. In addition, their improved durability and versatility make CPNC-based sensors suitable for deployment in diverse environments, contributing to their potential as advanced sensor materials. Polypyrrole, polyaniline (PANI), polythiophene, and their derivatives have been used as the active layers of gas sensors since the early 1980s [1].

The detection of harmful gases, such as volatile organic compounds (VOCs), is paramount for ensuring human and environmental health. Many VOCs are human-made chemicals that are used and produced in the manufacture of paints, pharmaceuticals, and refrigerants. VOCs typically are industrial solvents, such as trichloroethylene; fuel oxygenates, such as methyl tert-butyl ether; or by-products produced by chlorination in water treatment, such as chloroform. VOCs are often components of petroleum fuels, hydraulic fluids, paint thinners, and dry cleaning agents. Detection of VOCs is an essential need in both laboratories and industry for applications such as air-quality monitoring, controlled-industrial processing, and human safety. Various gas sensing technologies, such as gas chromatography, mass spectrometry, and gas sensors, are utilized to detect and quantify VOC concentrations effectively, enabling real-time monitoring and informed decision-making to address potential hazards and improve overall air quality.

Different varieties of VOC chemical sensors have been developed mainly for the detection of an analyte at any required concentration. Acetone is one of the most common VOCs, is dangerous, and may therefore easily damage the human body, i.e., eyes, nose, and nervous system when the concentration exceeds 170 ppm. Methanol also produces poisonous effects on nearly all organ systems, but the central nervous system, cardiovascular system, and respiratory systems are largely affected by methanol toxicity. In most cases, polymers are used as sensing materials for VOCs detection because they provide an excellent linearity of the sensor signal as a result of the physical sorption of the gas molecules. Furthermore, polymer films are known for their long-term stability and offer a good concession between response time, selectivity, and reversibility. Among various polymers that have been exploited as active layers for VOCs detection on gas sensors, organic acids doped PANI can enhance the sensing performance. One suitable candidate material for this sensor is the conducting polymer, which offers the advantage of room-temperature operation.

This review focuses on the overall development of conducting polymers as chemiresistive sensing materials. Commercially available sensors, which are based on metal oxides, operate at high temperatures, but the conducting polymer sensors have many improved characteristics like they show high sensitivities, short response time, at room temperature (RT). By chemical or electrochemical processes, conducting polymers are synthesized and their molecular chain structure can be modified conveniently by copolymerization or structural derivations. There are several reviews that emphasize different aspects of gas sensors [2-4], and some others discussed sensing performance of certain conducting polymers [5-7], but few of them paid special attention to recapitulating

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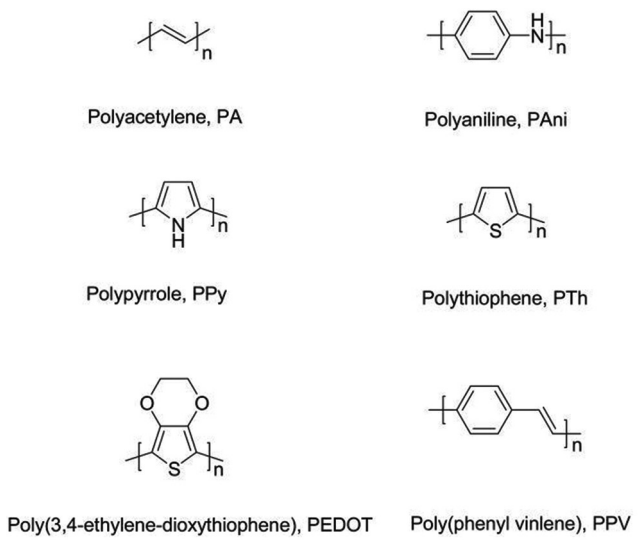
gas detectors grounded on different conducting polymers. The conducting polymers mentioned are all referring to intrinsic conducting polymers. Their main chain consists of indispensable single and double bonds, which leads to broad π-electron conjugation. Scheme 1 presents several typical conducting polymers used as the active layers in gas detectors. However, the conductivity of these pure conducting polymers is rather low ($<10^{-5}$ S cm^{-1} To achieve largely conductive polymers, doping process is necessary. Doping is the central theme which distinguished conducting polymers from all other polymers [8]. Conducting polymers can be doped by redox reaction or protonation, in which the latter is only applicable to PANI.

2. CONDUCTING POLYMERS AS SENSOR DEVICES

Polymer materials boast numerous advantages as sensor materials compared to other options in the majority of sensor technologies. Their lightweight nature makes them suitable for applications where weight is a concern, while their ease of synthesis allows for scalable production. Polymers also exhibit improved stability and are resistant to environmental factors, ensuring reliable sensor performance over time. Moreover, their non-toxic nature makes them safer to handle and dispose of compared to other materials. In addition, polymers can be tailored through structural and compositional modifications to exhibit specific functionalities, such as electrochemical activity or responsiveness to different stimuli. This versatility makes polymers indispensable for a wide range of sensor applications, from environmental monitoring to biomedical diagnostics, driving ongoing research in polymer science to further expand their capabilities.

The properties of polymers are intricately determined by their molecular structure, molecular weight, molecular weight distribution, and morphology. The arrangement of atoms and chemical bonds within the polymer chain, along with the presence of side chains or functional groups, dictates characteristics such as flexibility, rigidity, and chemical reactivity. While polymers typically exhibit electrical insulating properties due to the absence of free electrons, conducting polymers, as organic macromolecules, stand out for their ability to conduct electricity. This unique property arises from the presence of extended p-electron conjugation within their molecular structure. This extended conjugation allows for either ionic or electronic conduction, enabling conducting polymers to serve as efficient electrical conductors or semiconductors. By harnessing this distinctive feature, conducting polymers find application in various fields such as electronics, sensors, energy storage, and optoelectronics, contributing to advancements in technology and materials science.



Scheme 1: Types of Conducting Polymers.

The fabrication of polymeric sensor devices presents distinct advantages compared to metal oxide and ceramic semiconductor devices, as it eliminates the need for high temperatures and costly processing techniques. Conducting polymers offer ease of synthesis and fabrication, making them highly suitable for sensor applications. In the realm of chemical sensor research, there has been a notable shift toward developing miniaturized sensor arrays composed of nanostructured conducting polymers and composites. These advancements enable the selective detection of specific chemical analytes within complex mixtures, highlighting the potential of polymeric sensor technology in achieving precise and selective chemical sensing capabilities. This emphasis on miniaturization and nanostructuring underscores the ongoing innovation and progress in enhancing the performance and applicability of polymeric sensor devices in diverse fields.

The presence of unsaturated bonds in conducting polymers renders them reactive to oxygen or moisture, potentially compromising their stability in ambient environments or when exposed to certain analyte compounds. In addition to the inherent stability of the polymers themselves, the stability of dopants utilized in conducting polymers is crucial, as dopant molecules may also react with the surrounding environment. Furthermore, polymers must exhibit sensing functionality across a broad temperature range. In addition, polymers incorporated into sensor devices must possess adequate mechanical strength to endure various environmental conditions and handling processes. These considerations underscore the importance of addressing stability issues and ensuring robust mechanical properties when designing and utilizing conducting polymers in sensor applications.

3. SYNTHESIS OF CONDUCTING POLYMERS

Polymers exhibit a high degree of tailorability through modifications in their structures and compositions, allowing for enhanced processing behavior and the development of specific functional properties. This versatility is particularly advantageous in sensor applications, where polymers can be engineered to display redox behavior, possess charge-carrying capabilities, and respond to optical stimulation. The easy processability of polymers enables the formation of thin layers, facilitating the creation of compact and miniaturized sensor arrays. The flexibility inherent in polymer chains further contributes to the adaptability of sensor devices. By leveraging the customizable nature of polymers, artificial sensor devices with improved sensitivity and the ability to detect multiple analytes simultaneously can be readily fabricated, making them valuable in diverse fields ranging from environmental monitoring to healthcare.

Conducting polymers are commonly synthesized through chemical or electrochemical methods, both of which involve the oxidation of corresponding monomers. In chemical oxidation, the process typically entails mixing the monomer with an oxidizing agent in a solution. For example, in the case of PANI, the presence of a protonic acid is often necessary to ensure the production of a linearly structured polymer product. Chemical oxidation reactions enable the formation of polymer chains by initiating the polymerization process through the transfer of electrons. The choice of oxidizing agent and reaction conditions can influence the properties of the resulting conducting polymer. In the case of PANI, the protonic acid serves not only as an oxidizing agent but also as a dopant, influencing the conductivity and other properties of the final polymer product.

Electrochemical synthesis, on the other hand, involves the application of an electric potential to drive the oxidation and polymerization of

monomers directly on an electrode surface. This method provides better control over the polymerization process and allows for the fabrication of conducting polymers with specific properties. Both chemical and electrochemical methods are viable routes for synthesizing conducting polymers, and the choice between them often depends on factors such as the desired properties of the polymer and the specific application requirements.

The synthesis of conducting polymers involves the use of various oxidants, and among the most widely used are ammonium persulfate, ferric chloride, hydrogen peroxide, potassium dichromate, cerium sulfate, and others. These oxidants can be employed in both aqueous and organic media, providing flexibility in the synthesis process. In electrochemical synthesis, several methods are available, including galvanostatic, potentiostatic, cyclic voltammetry, and other potentiodynamic techniques. Regardless of the method chosen, a three-electrode system is commonly utilized for conducting polymer synthesis. This system comprises a working electrode, a counter electrode, and a reference electrode.

Various materials can serve as the working electrode in the synthesis of conducting polymers, including platinum, stainless steel, gold, and indium tin oxide glass. In many instances, the polymers deposited on the electrode surface can be peeled off into self-standing states, offering versatility in the fabrication process [9]. This flexibility in electrode material and the ability to produce freestanding polymer films contribute to the adaptability and wide applicability of conducting polymers in various technological and sensing applications.

4. PREPARATION OF CONDUCTING POLYMER FILMS

The preparation of conducting polymer films involves several methods, and the choice of technique depends on factors such as the specific conducting polymer, the substrate material, the desired film thickness, and the intended application of the conducting polymer film. Each technique offers unique advantages and can be tailored to meet specific requirements in terms of film quality and functionality.

4.1. Chemical Polymerization

a. Solution polymerization: Conducting polymers can be synthesized in solution, and the resulting polymer solution can be used to form films by techniques such as spin-coating, drop-casting, or dip-coating.
b. *In situ* polymerization: Polymerization occurs directly on the substrate, forming a conducting polymer film. This can be achieved by immersing the substrate in a monomer solution, followed by the addition of an oxidizing agent.

4.2. Electrochemical Polymerization

a. Galvanostatic or potentiostatic polymerization: An electric potential is applied to electrodes in a monomer solution, leading to the deposition of conducting polymers on the electrode surfaces. The choice of potential or current determines the thickness and properties of the resulting film.
b. Cyclic voltammetry: This method involves cycling the potential applied to the electrodes, resulting in the repeated formation and removal of the polymer film. It is useful for controlling film thickness and structure.

4.3. Layer-by-Layer Assembly

a. Conducting polymer films can be built layer by layer by alternately depositing oppositely charged polymers or polyelectrolytes. This technique allows precise control over film thickness and composition.

4.4. Chemical Vapor Deposition

a. Vapor-phase polymerization can be employed to deposit conducting polymer films. Monomer vapors are introduced into a reaction chamber, where they polymerize and form a thin film on the substrate.

4.5. Template-Assisted Methods

a. Templates, such as porous membranes, can be used to guide the growth of conducting polymers, resulting in films with specific structures and properties.

4.6. Spray Coating

a. A solution of the conducting polymer is sprayed onto the substrate, allowing for the formation of a uniform film. This technique is suitable for large-area coatings.

4.7. Langmuir-Blodgett Technique

a. This method involves the transfer of monolayers of conducting polymers from the air-water interface onto a solid substrate, producing well-organized films.

4.8. Inkjet Printing

a. Inkjet printing can be used to deposit conducting polymer inks onto substrates with high precision, enabling the fabrication of patterned films.

4.9. Electrospinning

a. Electrospinning is an efficient, relatively simple, and low-cost method for producing polymer and composite fibers with diameters ranging from several nanometers to a few micrometers. It is a versatile and widely used technique for fabricating nanofibers from various polymers and composite materials. The process involves the use of an electric field to draw and stretch a charged polymer solution or melt it into a fine fiber.

This review article employs polyacrylonitrile (PAN) fibers, crafted through the electrospinning technique. Following electrospinning, the nonwoven membranes of PAN nanofibers undergo a drying process at 600°C. Subsequently, PANI is synthesized through a chemical oxidation method. The PAN nanofibers, prepared earlier, are then utilized to coat PANI, resulting in the formation of PANI/PAN blend nanofibers using a dip coating process coupled with *in situ* chemical oxidative polymerization.

A polymer solution or melt is prepared by dissolving a polymer in a suitable solvent. The choice of polymer and solvent depends on the desired properties of the final nanofiber. The polymer solution is loaded into a syringe, which is connected to a micro-syringe pump. The pump controls the flow rate of the polymer solution. The syringe is equipped with a metallic needle (spinneret) at its tip. The spinneret is connected to a high-voltage power supply. A grounded collector is positioned at a specific distance from the spinneret. When a high voltage is applied to the polymer solution at the spinneret, electric charges are induced on the surface of the droplet. The repulsion of like charges and the attraction to the grounded collector cause the polymer solution to form

a conical shape known as a Taylor cone. As the electric field strength increases, a fine jet of the polymer solution is ejected from the Taylor cone. This jet undergoes a whipping or bending instability due to the electrostatic forces, resulting in the formation of a thin, continuous fiber. During the flight toward the grounded collector, the solvent evaporates, leaving behind a solid nanofiber. If the process involves a polymer melt, the fibers solidify upon contact with the collector. The collector can be in the form of a rotating drum, a stationary plate, or other configurations. The collector choice influences the alignment, density, and orientation of the nanofibers.

5. GAS SENSING

Gas sensors play a crucial role in detecting and measuring the concentration of various gases in the surrounding environment. These devices are designed to respond to specific gases, providing valuable information for monitoring air quality, ensuring workplace safety, and detecting potential hazards. Gas sensors find applications in diverse fields, including industrial processes, environmental monitoring, healthcare, and home safety systems.

In recent years, there has been a surge in research focusing on the development and characterization of conducting polymeric nanocomposites tailored for a diverse array of sensing applications. These innovative materials hold significant promise in fields ranging from chemical and biological sensing to mechanical sensing. By integrating conducting polymers with nanomaterials, such as nanoparticles or nanofibers, researchers aim to enhance sensor performance by leveraging the unique properties of both components. These conducting polymeric nanocomposites offer advantages such as improved sensitivity, selectivity, and stability, paving the way for the development of next-generation sensing devices with enhanced capabilities. The continued exploration and refinement of these materials underscore their potential to revolutionize sensing technologies across various industries and applications.

5.1. Types of Gas Sensors

Gas sensors are typically classified into various types based on the type of sensing element it is built with. Based on the concentration of the gas, the sensor produces a corresponding potential difference by changing the resistance of the material inside the sensor, which can be measured as output voltage. Based on this voltage value, the type and concentration of the gas can be estimated. Below is the classification of the various types of gas sensors based on the sensing element that is generally used in various applications.

5.2. Electrochemical Gas Sensors

These sensors operate on the basis of electrochemical reactions between the target gas and an electrolyte. The electrochemical gas sensor operates by facilitating electrochemical reactions at its electrodes to measure the concentration of a specific target gas. As the gas diffuses into the sensor through a porous membrane, it reaches the working electrode, where oxidation or reduction occurs, generating an electric current proportional to the gas concentration. Simultaneously, the external circuit maintains the voltage across the sensor between the working and counter electrodes, ensuring proper functioning. Common applications of electrochemical gas sensors include the detection of oxygen, carbon monoxide, carbon dioxide, ammonia, hydrogen cyanide, and hydrogen sulfide. These sensors find widespread use in industries such as agriculture, food, and oil, as well as in environmental and biomedical applications. Known for their sensitivity, selectivity, and cost-effectiveness, electrochemical gas sensors provide a convenient solution for the detection of variable analytes in diverse settings.

5.3. Metal Oxide Semiconductor (MOS) Gas Sensors

MOS gas sensors are widely used for the detection of various gases in different applications. These sensors operate on the principle of changes in the electrical conductivity of a MOS material when exposed to specific gases. The basic structure of a MOS gas sensor typically consists of a thin film of metal oxide material deposited on a substrate, forming a semiconductor element. MOS sensors detect changes in the electrical conductivity of a MOS when exposed to gases. Widely used for detecting gases such as methane (CH_4), propane (C_3H_8), and various VOCs. When the MOS is exposed to a target gas, the gas molecules adsorb on the surface of the semiconductor, leading to changes in its electrical conductivity. The interaction between the gas and the semiconductor causes a change in the resistance or conductance of the material, which can be measured and correlated with the gas concentration. Common metal oxides used in these sensors include tin oxide (SnO_2), zinc oxide (ZnO), and tungsten oxide (WO_3). Fast response time and suitable for detecting a range of gases for their applications range from industrial safety to environmental monitoring, contributing to enhanced safety and quality of life in various settings.

5.4. Catalytic Bead (Pellistor) Gas Sensors

Catalytic bead, also known as pellistor, gas sensors are widely used for the detection of combustible gases in diverse industrial applications. These sensors operate on the principle of catalytic combustion, relying on the heat generated by the combustion of gases on a heated bead. These sensors contain a bead made of a catalytic material, often platinum or palladium, which is heated to a specific temperature. When combustible gases come into contact with the catalytic bead, they undergo a catalytic combustion reaction on the surface of the bead, releasing heat. The heat generated by the combustion reaction causes a change in the temperature of the catalytic bead, which is proportional to the concentration of the combustible gas. The change in temperature results in a change in the electrical resistance of the catalytic bead, which is measured and correlated with the gas concentration. These sensors use the catalytic combustion of gases on a heated bead to detect combustible gases. Commonly used for detecting flammable gases such as methane, propane, and hydrogen.

5.5. Infrared Gas Sensors

Infrared gas sensors operate on the principle of measuring the absorption of infrared radiation by specific gases. These sensors are designed to detect and quantify the concentration of gases based on their characteristic absorption spectra in the infrared region. Different gases have unique absorption bands in the infrared spectrum. Infrared gas sensors typically focus on specific wavelengths corresponding to the absorption bands of the target gases. When infrared radiation passes through or interacts with a gas sample, the gas molecules absorb specific wavelengths of the infrared light. The remaining infrared radiation is detected by a detector, and the sensor measures the difference between the emitted and received infrared light to determine the gas concentration. Infrared sensors operate by measuring the absorption of infrared radiation by specific gases, used for detecting gases like carbon dioxide (CO_2), methane, and hydrocarbons.

5.6. Photoionization Detectors (PID)

PIDs are gas sensors that operate based on the principle of photoionization. These detectors are commonly used to measure the concentration of VOCs and other gases that can be ionized when exposed to ultraviolet (UV) light. Here's an overview of the working principle, applications, and characteristics of PIDs. Photoionization Detectors use UV light to ionize gas molecules in the sample. When the UV light strikes the gas molecules, it causes the ejection of

electrons, resulting in the formation of positively charged ions. The generated ions contribute to an electric current, and the magnitude of this current is proportional to the concentration of the ionizable gas. PID sensors ionize gas molecules using UV light, and the resulting current is measured. Commonly used for detecting VOCs and other hazardous substances.

5.7. Semiconductor Gas Sensors

Semiconductor gas sensors are devices that utilize the electrical conductivity of semiconducting materials to detect the presence of various gases. These sensors are commonly used in a wide range of applications, including industrial safety, environmental monitoring, and gas leak detection. Used for detecting gases such as hydrogen (H_2), ammonia (NH_3), and sulfur dioxide (SO_2).

5.8. Piezoelectric Gas Sensors

Piezoelectric gas sensors are devices that utilize the piezoelectric effect to detect the presence of gases. The piezoelectric effect refers to the generation of an electric charge in certain materials when they undergo mechanical stress. These sensors are commonly used in gas detection applications due to their sensitivity and ability to respond to changes in pressure caused by gas interactions. Used for detecting gases such as methane and propane.

5.9. Surface Acoustic Wave (SAW) Gas Sensors

SAW gas sensors are devices that use the piezoelectric effect on the surface of a material to detect changes in acoustic waves caused by the interaction with gases. These sensors are known for their high sensitivity and selectivity, making them suitable for detecting specific gases in various applications. Commonly used for detecting gases such as ammonia, nitrogen dioxide (NO_2), and sulfur dioxide.

This classification highlights the diversity of gas sensor technologies, each suitable for specific applications based on factors such as sensitivity, selectivity, response time, and cost. Choosing the right type of gas sensor depends on the target gas and the requirements of the application.

The use of PANI-based nanocomposites has demonstrated remarkable sensing capabilities toward a wide range of gases and VOCs including NH_3, H_2, HCl, NO_2, H_2S, CO, CO_2, SO_2, liquefied petroleum gas (LPG), and VOCs. Subsequently, pertinent information from related studies such as detection limits, sensing ranges, response times (tres)/recovery times (trec), repeatability, and stability are carefully summarized and discussed. These sensitivities have been leveraged in the development of novel sensor technologies.

6. PANI-BASED NANOCOMPOSITE FOR GAS DETECTION

The development of gas sensor technology has received considerable attention in recent years for monitoring environmental pollution. It is well-known that chemical gas sensor performance features such as sensitivity, selectivity, time response, stability, durability, reproducibility, and reversibility are largely influenced by the properties of the sensing materials used [10-12]. Many kinds of materials such as polymers [13,14], semiconductors [15,16], carbon graphites [17,18], and organic/inorganic composites [19,20] have been used as sensing materials to detect the targeted gases based on various sensing techniques and principles. It is worth noting that the sensitivity of chemical gas sensors is strongly affected by the specific surface of sensing materials [21,22]. A higher specific surface of a sensing material leads to a higher sensor sensitivity, therefore, many techniques [23-25] have been adopted to increase the specific surface of sensing films with fine structures, especially to form the nanostructures, taking advantage of the large specific surface of nanostructured materials.

Kumar *et al*., [26] presented an NH_3 gas sensor employing chemically synthesized gold nanostars (AuNS) as catalysts, demonstrating their ability to enhance the sensing activity of insulating PANI thin films. They observed that the incorporation of AuNS resulted in increased sensitivity toward NH_3 at the same concentration level compared to utilizing other gold nanostructures such as gold nanorods (AuNR) and spherical gold nanoparticles (AuNPs). This finding underscores the importance of catalyst selection and nanostructure morphology in optimizing the performance of PANI-based gas sensors for NH_3 detection.

Sadek *et al*. [27] reported the chemical polymerization technique for the fabrication of PANI/WO_3 nanocomposite on the surface of a layered ZnO/64 YX $LiNbO_3$ substrate for monitoring H_2 gas. The study observed that the PANI/WO_3 nanocomposite sensor consistently generates repeatable responses of the same magnitude, indicating excellent reproducibility in its sensing performance.

Sharma *et al*. [28] utilized the electrospinning technique to fabricate Al-doped SnO_2 (AleSnO_2)/PANI composite nanofibers for hydrogen (H_2) sensing. Experimental results indicated that the 1% AleSnO_2/PANI nanofibers exhibited a superior response to hydrogen compared to 1% AleSnO_2 alone. Specifically, the 1% AleSnO_2/PANI hybrid demonstrated high sensitivity (~275%) to H_2 gas (at 1000 ppm) at a temperature of 48°C, with relatively fast response (2 s) and recovery times (2 s).

Furthermore, Srivastava *et al*. [29] reported on the development of an interdigitated electrode-based chemiresistor-type gas sensor, focusing on thin films of PANI and carbon nanotube (CNT)-doped PANI for H2 gas sensing at RT. Gas sensing measurements were conducted toward a 2% hydrogen concentration in air at 1.3 atm hydrogen pressure at RT. The response of the PANI film was measured at around 1.03, which increased to 1.06 and 1.07 for multi-walled CNT/PANI and single-walled CNT/PANI composite films, respectively.

Mishra *et al*. [30] developed a highly specific, rapid, and sensitive hydrogen chloride (HCl) gas sensor utilizing nanocomposites of copolymers of aniline (ANI) and formaldehyde (HCHO). These

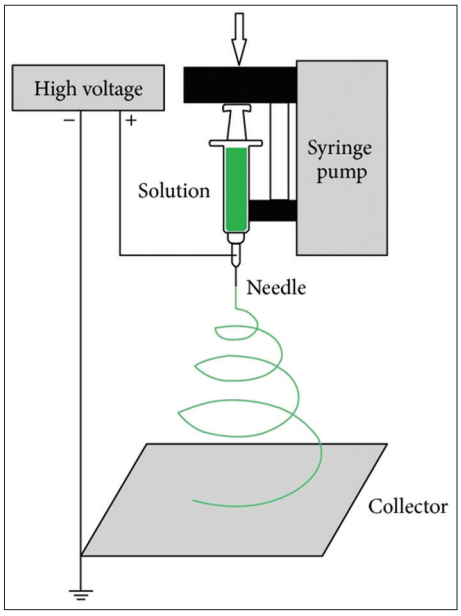


Figure 1: Electrospinning setup. AQ5

nanocomposites were prepared with a metal complex of FeAl (in a ratio of 95:05) using thermal vacuum evaporation deposition techniques. The sensor demonstrated the capability to detect HCl gas concentrations ranging from 0.2 to 20 parts per million (ppm) within 8–10 s.

Xu *et al*. [31] presented a novel approach for nitrogen dioxide (NO_2) sensing using a SnO_2-ZnO/PANI composite thick film. The composite material was fabricated by combining SnO_2-ZnO porous nanosolid with PANI using a conventional coating method. The SnO_2-ZnO composite porous nanosolid was synthesized via a solvothermal hot-press technique. The study observed that the sensor based on the SnO_2-ZnO/PANI composite exhibited remarkable stability when exposed to NO_2 at a concentration of 35 parts per million (ppm) for 22 min at a temperature of 180° Celsius.

Sen *et al*., [32] presented PANI/ferric oxide (PANI/Fe_2O_3) nanocomposite films for the detection of LPG at RT. The PANI/Fe_2O_3 nanocomposite films were investigated for their response to LPG within the concentration range of 50–200 parts per million (ppm). The maximum response observed for PANI/Fe_2O_3 (3 wt%) nanocomposite films to 50 ppm LPG was reported to be 0.5%, with a response time of 60 s.

Athawale *et al*. [33] developed a nanocomposite comprising PANI and palladium (Pd) specifically designed for the detection of methanol. The experimental findings demonstrated an exceptionally high response level, on the order of approximately 104 magnitudes, for the detection of methanol at a concentration of 2000 parts per million (ppm).

7. THE SENSING MECHANISM OF CONDUCTING POLYMER SYNTHESIZED BY ELECTROSPINNING

Various methods have been utilized to construct these architectures, with electrospinning standing out due to its simplicity in preparation, cost-effectiveness, suitability for mass production, and adaptability, enabling control over both fiber diameter and the final properties of the fibrous structure. Moreover, this technique allows the precise deposition of micro-/nanofibers onto any type of flexible electrode with high reproducibility. Furthermore, depending on the precursor materials employed in conjunction with appropriate post-treatments, it is possible to successfully fabricate flexible, free-standing, and all-solid-state micro-nanofiber architectures.

PAN nanofibers are prepared using the electrospinning method. Prepared PAN nanofibers were used for coating PANI to form PAN/PANI blend nanofibers using dip coating *in situ* chemical oxidative polymerization process.

The synthesized PANI/PAN blend nanofibers were used as the receptor for analyte gas molecules. Exposure of the fabricated PANI/PAN sensor showed that an increase in the resistance with increasing temperature was observed for methanol and acetone. The PANI layer in the blend acts as the active sensing layer and shows changes in the resistivity on the adsorption of the analyte gas molecules. The sensitivity of PANI/PAN sensor calculated for both methanol and acetone gas for different concentrations is shown in Figures 2 and 3, respectively. It was observed that the sensitivity of the sensor increases for higher concentrations of methanol and acetone. It is worth mentioning that the sensitivity is highest at near RT although the working temperature slightly differs with concentrations. Furthermore, the sensitivity of the sensor increases with increasing concentration of methanol and acetone.

The sensing mechanism is found to be governed by protonation and deprotonation phenomena. The resistivity of the blend increases in the presence of methanol due to the reduction or undoping of charge

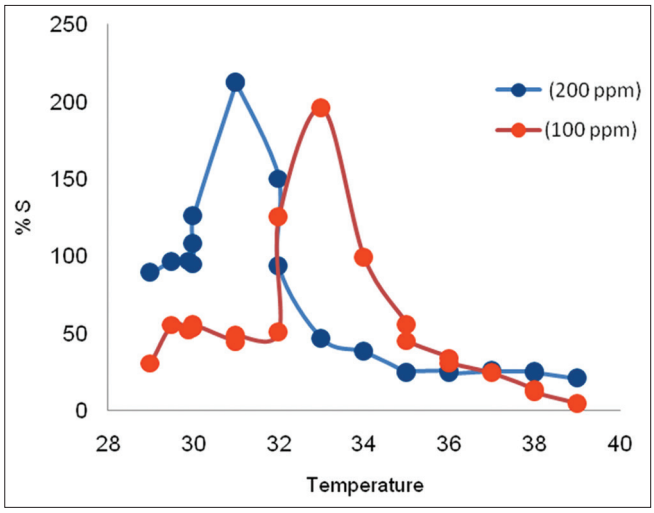


Figure 2: Sensitivity of the polyaniline/polyacrylonitrile blend sensor for methanol at different concentrations.

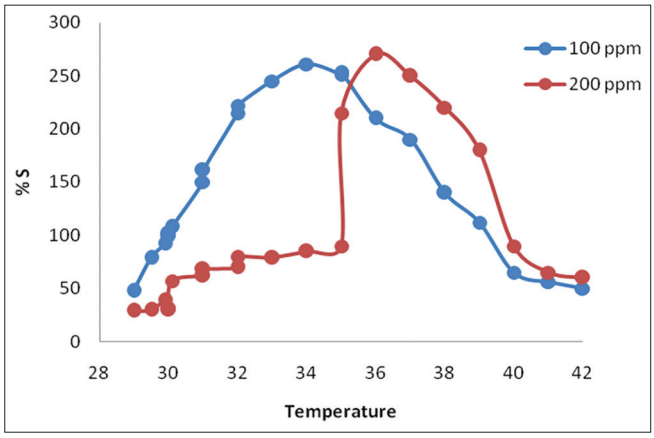


Figure 3: Sensitivity of the polyaniline/polyacrylonitrile blend sensor for acetone at different concentrations.

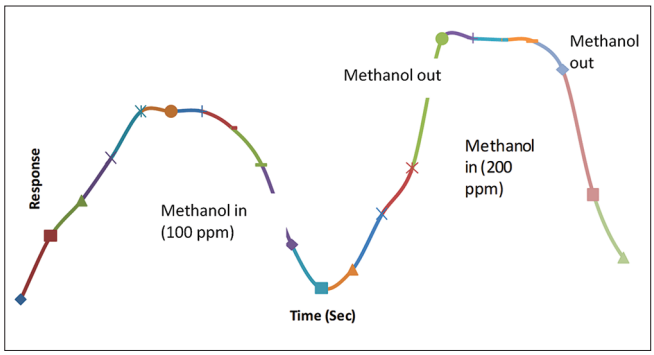


Figure 4: Response and recovery of polyaniline/polyacrylonitrile blend sensor for methanol at different concentrations.

carriers by the adsorption of methanol on the surface of the blend. The sensitivity factor was found to be 195 and 212 for 100 ppm and 200 ppm of methanol, respectively, at temperatures of 31°C and 33°C, respectively. For acetone, the sensitivity factor was obtained as 261 and 270 for 100 ppm and 200 ppm at temperatures of 34°C and 36°C, respectively. A plot of response (Rg/Ra) and recovery of the sensor for the analyte gases methanol and acetone with respect to time is shown in Figures 4 and 5, respectively. It can be seen that the response of the sensor increases with increasing concentration of methanol as well as

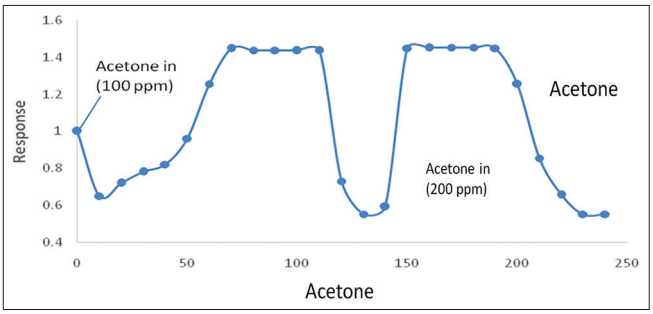


Figure 5: Response and recovery of polyaniline/polyacrylonitrile blend sensor for acetone at different concentrations.

Table 1a: Comparison of the sensitivity, response time, recovery time, and operating temperature of as-synthesized PANI/PAN blend nanofibers for methanol.

Sensing materials	Operating temperature (°C)	Sensitivity (S%)	Response time (s)	Recovery time (s)
PANI/PAN blend	33°C	212	10 s	50 s

PANI/PAN: Polyaniline/polyacrylonitrile

Table 1b: Comparison of the sensitivity, response time, recovery time, and operating temperature of as-synthesized PANI/PAN blend nanofibers for acetone.

Sensing materials	Operating temperature (°C)	Sensitivity (S%)	Response time (s)	Recovery time (s)
PANI/PAN blend	36°C	270	20 s	20 s

PANI/PAN: Polyaniline/polyacrylonitrile

acetone with the highest response for 200 ppm of acetone.

8. SENSING MECHANISM

Since HCl is used as a dopant during polymerization in this work, PANI is obtained in the form of emeraldine salt. When exposed to methanol during sensing, the HCl molecule donates H+ ions to the PANI chain, thus increasing the number of positively charged carriers in the material. The process is termed as protonation and gives bipolarons due to excess doping of PANI and results in decrease in the electrical resistivity of the sensor. With the increasing concentration of the analyte methanol, the sensitivity is increased which is attributed to the diffusion of more methanol molecules into the fiber at higher concentration which can be concluded from [Table 1a]. On the other hand, when the sensor is exposed to the acetone, deprotonation takes place. Acetone molecules of gas take up the hydrogen atom from the PANI chain and form NH_4^+ ammonium ions. The emeraldine salt form of the PANI thus changes into the emeraldine base form with decrease in the number of carriers. This leads to an increase in the electrical resistivity of the sensor and decrease in the number of polarons. Here too, the sensitivity is found to increase with the increasing concentration of the acetone which indicates that more acetone molecules diffuse into the fiber at higher concentration which can be concluded from [Table 1b]. The response and recovery time are defined as the time to reach 90% of the resistance change during exposure and on removal of gas, respectively.

9. CONCLUSION

PANI/PAN blend nanofibers have been synthesized successfully by electrospinning and dip-coating polymerization. The studies of PANI/PAN blend as a sensor for methanol and acetone show sensitivity which increases with the increasing concentration of both gases. The operating temperature of PANI/PAN blend for methanol as well as acetone gas sensor was found to be near RT. These results, along with low response time, confirmed the possible use of the prepared material as a potential candidate for the sensing of methanol and acetone in environmental monitoring safety systems, chemical industry, automotive industry, and medical application areas. Thus, the combination of conducting polymers with nanomaterials in nanocomposites brings forth a range of desirable properties, making promising materials for sensor devices with design pliability, good sensitivity, and low-temperature operation. These features open up avenues for innovation in sensor technology across various fields, including environmental monitoring, healthcare, and industrial applications.

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