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Electrospun Based Polyaniline Sensors – A Review

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Abstract. Polyaniline is a polymer with outstanding electronic conductivity and good response to molecules at room temperature. This review focuses on the many uses of electrospun polyaniline nanofibers as chemical sensor with high sensitivity and functionality, providing a concise report of the present status of polyaniline gas sensing applications. Latest developments in this area are reported and the capability of PANI sensors to detect various gases is emphasized. Difficulties that may obstruct practical uses of these sensors are also summarized.

1. Introduction

Many conducting polymers, such as polyaniline (PANI), poly (paraphenylen), polythiophene, poly (paraphenylenvinylen), polypyrrole, poly (3,4-ethylene-dioxythiophene), have been used in gas sensing from more then 30 years [1-5]. The conducting polymer based sensors prove to have many improved characteristics in comparison with the sensors usually based on metal oxides, and their capability to operate at room temperature is one of the most important [6-9]. Polyaniline, with a unique structure that allows it to exist in five oxidation states (figure 1), raise a special interest due to the ease of its synthesis and its versatility as sensor [10].

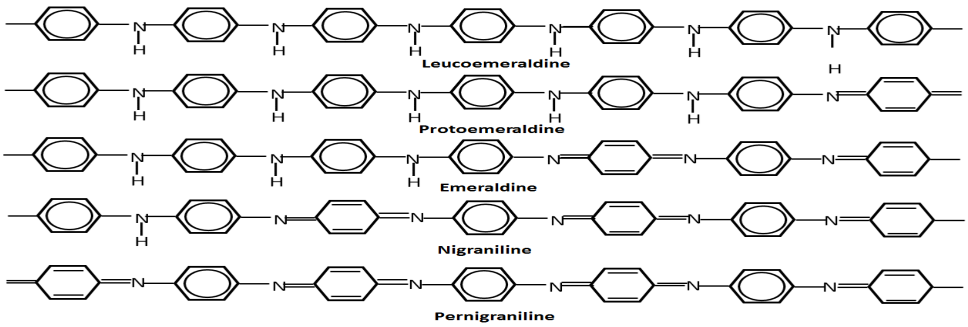

Figure 1. The five oxidation states of polyaniline.

None of the oxidation states of PANI are conductive, but protonated forms of the moderately oxidized states, especially emeraldine, are conductive [11-14]. The protonic acid doping process of PANI is illustrated in figure 2.

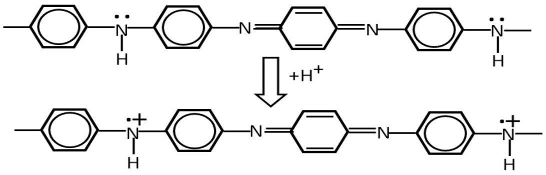

Figure 2. Protonic acid doping process of polyaniline.

2. Polyaniline as pH sensor

Polyaniline, as all the conductive polymers, has groups which can be protonated or deprotonated. Deprotonation leads to a decrease of charge carriers along the polymer chains, followed by variations in the electrical properties and modification of redox properties of PANI [1,15-18]. Polyaniline is suitable for pH sensing in aqueous medium, because conductivity decreases rapidly with increase in pH at a given potential. Optical pH sensors, based on polyaniline films prepared by chemical oxidation at room temperature, showed improved stability. The effect of pH on the change in electronic spectrum of polyaniline polymer can be explained on the basis of different degree of protonation of the imine nitrogen atoms in the polymer chain. The pH of solution could be determined by monitoring either absorption at a fixed wavelength or maximum absorption wavelength of the film. The sensor can be kept exposed in the air for over one month without any deterioration in sensor performance [19]. A polyaniline based amperometric pH sensor has been obtained using a polyaniline film coated pencil graphite electrode which is connected in series between the working and counter electrodes of a potentiostat, and immersed in the solution together with a reference electrode. When an external potential is applied, the resulting current varies with the pH solution, which provides the basis for the amperometric pH sensor [20].

3. Polyaniline for inorganic gaseous analytes detection

Gases interact with polyaniline in two ways: by a chemical reaction, such as nitrogen dioxide, sulphur dioxide, ozone, hydrogen, hydrazine, hydrochloric acid, ammonia, hydrogen sulphide, or by adsorption, such as chloroform, dichloromethane, acetonitrile, many alcohols, benzene, acetone [1].

3.1. PANI based ammonia sensors

Ammonia is a colourless gas with a suffocating odour. In case of inhalation, ingestion (solution) or skin and/or eye contact (solution/liquid), ammonia causes various health-related issues, such as dyspnea (breathing difficulty), irritation of eyes, nose and throat, chest pain and pulmonary edema. This is why The Occupational Safety and Health Administration (OSHA) have specified a threshold limit value for NH_3 in the workplace of 50 ppm [21]. Due to the dangerous effects of ammonia on human health and environment, it is absolutely necessary to monitor its trace level. To detect ammonia, electrospun nanofibres of PANI-PEO mixture which was doped with camphorsulfonic acid 10 (HCSA) were deposited on gold electrodes. The obtained sensor reacts with ammonia and alters its electrical resistance (figure 3), displaying a detection threshold of 0.5 ppm of NH_3. In figure 3, the normalized resistance [(R / Ro) - 1] is plotted as a function of analyte concentration [22]. The primary mechanism for detecting is the PANI deprotonation by ammonia, which results in an increase in resistance [23]. A field effect transistor (FET) based on polyaniline nanofibers obtained by electrospinning acts as a sensor for ammonia [24], presenting a reversible resistance change of 7% to 1 ppm NH_3 with a threshold voltage of 10 V. The diagram of the sensor is shown in figure 4.

A hybrid material based on nanostructured polyaniline and titanium dioxide [PANI-TiO_2] proved particularly effective in the detection of ammonia [25].

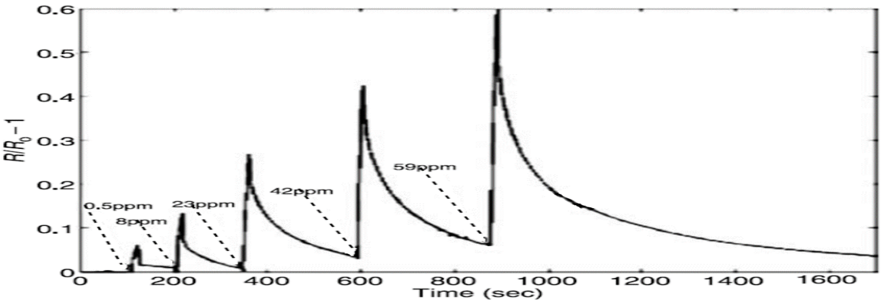

Figure 3. Real-time response of a PANI/PEO sensor to different concentrations of NH_3 gas.

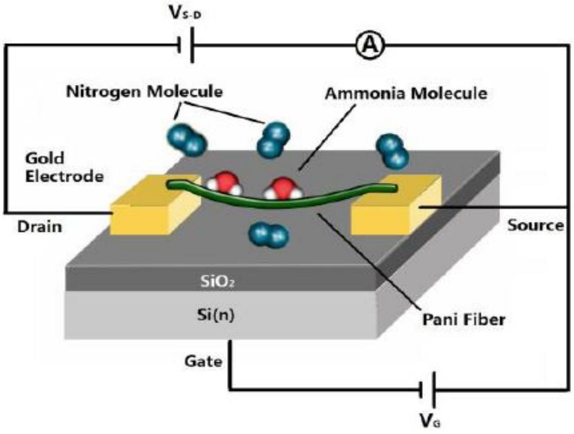

Figure 4. The diagram of the single polyaniline nanofiber field effect transistor sensor [24].

Its high sensitivity for NH_3 gas as compared to the other gases (CH_3OH, C_2H_5OH, NO_2, H_2S) was attributed by the authors to the high affinity for electrons of ammonia compared to the other gases. In order to overcome the difficulties of processing PANI, continuous + camphor-10-sulfonic acid [HCSA] doped PANI nanofibers were successfully produced by coaxial electrospinning with subsequent removal of the polymer shell and the system behaves as a sensor for both ammonia and nitrogen dioxide, showing high sensitivity and fast response time. However, resistive response for the two gases is quite different, being up to six orders of magnitude for NO_2 and less than two orders of magnitude for ammonia [26].

Electrospun PANI and PANI / ZnO nanofibers were used for the detection of NH_3 and HCl vapour at room temperature, and it was observed a decrease in resistance of the sensor on exposure to HCl vapour and an increasing resistance when exposed to NH_3 vapour. It has been found that the PANI / ZnO based sensor shows high response and sensitivity at room temperature, with very good reproducibility, in comparison with the sensor of pure PANI [27]. Contact sensors for the detection of ammonia have been obtained from mixtures of PANI electrospun nanofibres doped with HCSA and PEO that were sprayed over with gold microelectrodes. It has been observed that increasing the PANI content in the polymer mixture the sensitivity of the sensor increases, but the melting of the nanofibres significantly reduces the detection performance. Measuring conductivity vs. temperature showed that the electrons in the nano-fiber-based composite materials PANI / PEO are transported in a three-dimensional matrix [28]. Nanofibres from mixtures of PANI / poly-3-hydroxybutyrate (PHB) have been deposited by electrospinning on chemiresistors in order to investigate the effect of humidity on the ability of the sensors to detect ammonia and VOCs. It was found that the specific structure of the coating nanofibers and the physico-chemical properties of PANI / PHB allow the detection of ammonia and volatile organic compounds at high percentages of moisture, with low response time [6].

In_2O_3 / PANI nanofibers based sensors had a higher ammonia detection sensitivity than pure PANI at room temperature. The results indicated that In_2O_3 / PANI electrospun nanofibres based sensor has excellent selectivity, good repeatability and reversibility. The increased performance of the sensor for detecting ammonia can be attributed to the formation of p-n junctions between In_2O_3 and PANI [29].

A polyaniline nanofibers based sensor was tested at 100 ppm HCl and NH_3 vapour respectively. After exposure to HCl vapour the resistance of the polyaniline nanofibres decreases as a result of the doping process, and the ammonia exposure led to the de-doping process which increases the resistance of the polymer. The results showed that the sensor based on nanofibers has a much quicker response than the film-based sensor both for doping and de-doping, due to the morphology of the porous layer of nanofibres with small diameter which causes a rapid diffusion of the gas molecules [30].

3.2. PANI based nitrogen oxides (NOx)sensors

The most significant nitrogen oxides are nitrogen monoxide (NO) and nitrogen dioxide (NO_2). NO_2, which is released mainly from the combustion of fossil fuels, causes harmful effects on human health and the environment. As NO_2 is an irritant and an oxidant, which produces inflammation and oedema of the lungs if inhaled in high concentrations [31], the United States Environmental Protection Agency sets a one hour NO_2 standard at the level of 100 ppb.

Mixtures of PANI / poly (vinyl pyrrolidone) containing urease have proved to be suitable as NO_2 sensors [32,33]. Even for the basic form of polyaniline it can be measured an increase in the conductivity of the matrix in the presence of low levels of NO_2 (1-7 ppm). The answer to NO_2 in the presence of relative humidity (25% and 40%) for mixtures containing 20% wt./vol. and 80% wt./vol. PANI is substantially significant, and the amplitude of the response is an order of magnitude higher in the first case [32]. The equation for the relative sensitivity is given by:

$$S = \frac{|\Delta R|}{R_o} \cdot 100 \tag{1}$$

where ΔR is the change in resistance when exposed to the analysed gas and Ro is the baseline resistance (prior to exposure). For 5 ppm NO_2 exposures, the relative sensitivity for blends with 20% wt./vol PANI is 45% and only 9.5% for 80% wt./vol PANI mixtures. During the exposure NO_2 oxidizes PANI, which leads to an increase in the conductivity of PANI. PANI concentrations tested in these experiments ranged between 50% - 80% and 20% wt / vol [32]. These results contradict earlier research [34], which indicated that an increased of the share of PANI is favourable to increasing sensor sensitivity for NO_2 detection.

A chemiresistive sensor produced via potentiostatic deposition of a thin film of PANI on a n-octadecyl triclorosilan microelectrode was exposed to NH_3 and NO_2 and proved to have a sensitivity of 21% / ppm for NH_3 and 3760% / ppm for NO_2 and good reproducibility (sensitivity was defined as the slope of the linear range of the calibration curve). By adsorption of NH_3 on PANI the formation of ammonium ion is induced, producing the de-doping of emeraldine base to emeraldine which leads to a decrease in sensor conductivity. The detection limit for the ammonia, defined as three times the standard deviation divided by the slope of the control, was about 35 ppm [35].

A SnO_2-ZnO/PANI composite thick film obtained by coating method was used for detecting NO_2, showing high stability to NO_2 (35 ppm) at 180°C. The sensor response decreases at temperatures higher then 180°C. Despite the fact that the sensor response of analytes like NH_3, H_2, C_2H_5OH and CO was below 3%, the sensor showed a very high response of 368.9 on NO_2 [36]. A double-layered film SnO_2/PANI showed high selectivity and high response to NO_2 gas even at low concentration, with sensor response of 1-13% from the concentration range of 5-55 ppm of NO_2 and high reproducibility up to four cycles [37].

3.3. PANI based hydrogen sensors

Hydrogen, an odourless and colourless gas, is very explosive in a wide concentration range (4-75%) and has high permeability through many materials, motives enough for the development of hydrogen sensors to detect any leakage [38]. There are studies showing that hydrogen interacts directly with doped PANI nanofibers to induce a slight change in their conductivity [39, 40]. Direct uptake of hydrogen into PANI nanofibres was also observed using a quartz crystal microbalance (about 3% by mass of nanofibres). A plausible mechanism of hydrogen / doped PANI interaction involves the action of hydrogen on the charged nitrogen atoms, followed by the dissociation of the hydrogen with the formation of new NH links to the amino nitrogen of the PANI chain. Subsequently, polyaniline is returned at the initial doping state (emeraldine salt form) by charge transfer between adjacent atoms, with hydrogen release. Palladium nanoparticles doped polyaniline electrospun nanofibers were used to obtain a chemiresistor to detect hydrogen, registering a 1.8% variation of the resistance under a hydrogen concentration of 0.3% [41]. A solution that was obtained by adding SnCl2□2H2O to a solution of polyaniline in dimethylformamide (DMF) and ethanol under vigorous stirring and mixing it with polyvinylpyrrolidone was electrospun to obtain nanofibers that proved to have enhanced hydrogen detection properties at very low temperature compared to SnO_2 nanofibres [42]. Composite Al-SnO_2 / PANI electrospun nanofibres were used to detect hydrogen, yielding better results than in the case of a sensor based exclusively on the Al-SnO_2. The sensor has high sensitivity (~ 275%) in H_2 (1000 ppm) at 48°C [43]. A PANI/TiO_2:SnO_2 nanocomposite deposited onto an epoxy glass substrate was used to detect hydrogen at 27^oC with a sensitivity of 1.25 (0.8 vol% H_2) [44]. A chitosan/PANI composite was used to detect hydrogen and showed high sensitivity and high selectivity, and the sensor response to concentration between 0.3 to 4% was linear [45].

3.4. PANI based hydrogen disulphide sensors

Hydrogen sulfide (H_2S) is a flammable and extremely hazardous gas; even low concentrations of H_2S can cause eyes and respiratory system irritation, while high concentrations may cause shock, inability to breathe and even death. Threshold limit for H_2S in the workplace established by OSHA is 20 ppm, and therefore monitoring is very important [2].

A sensitive and selective chemiresistive sensor for detecting hydrogen sulphide at room temperature consists of polyaniline nanofibers electrochemically functionalized with gold nanoparticles using the cyclic voltammetry technique.

Hydrogen sulphide is a weak acid and therefore does not interact significantly with PANI and its electrical conductivity is not significantly changed, but when the PANI nanofibers network is functionalized with gold nanoparticles (70-120 nm in size) by electrodeposition, the hybrid sensor demonstrates an excellent response even at low concentrations of 0.1 ppb, a dynamic range of from 0.1 to 100 ppb and very good selectivity and reproducibility (figure 5) [46].

PANI / Ag films (about 0.5 M $AgNO_3$) were analysed in terms of their chemiresistive gas detection properties; when exposed to concentrations of 10 ppm of different gases, the sensors have produced a suitable response only for H_2S.

There is an increase of the current through exposure instead of a decrease that would be expected given the electron donor nature of the H_2S (reducing gas). The reason for this effect is the dissociation of H_2S on the metal surface, resulting H^+ and HS^-. While the anion compensates the N^+ charge in the polymer chain of the PANI, H^+, whose mobility is much higher than that of the anion, provides the observed conductivity.

Further evidence of this mechanism arises from the fact that, in the presence of high concentrations of Ag, the PANI matrix, which determines the change of conductivity upon exposure to H_2S, is significantly reduced. Features such as a detection limit of 1 ppm and fast response time make this composite to be a good candidate for H_2S gas detection [47].

PANI nanofibers functionalized with gold nanoparticles are also useful in the detection of volatile sulphur compounds in human breath. Sensors made by a redox reaction between $HAuCl_4$ and PANI in emeraldine form show a good response to gases such as H_2S and CH_3SH [48].

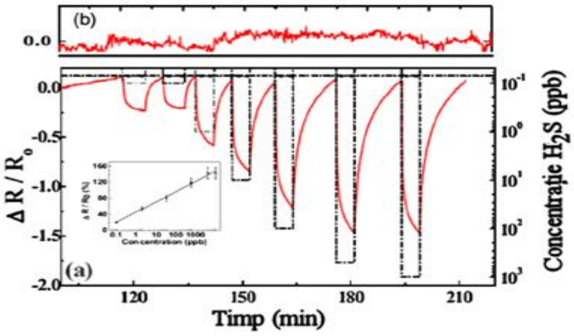

Figure 5. Response and recovery transients (solid line) of gold nanoparticles functionalized PANI nanowire network based chemiresistive sensor toward 0.1 ppb, 1 ppb, 10 ppb, 100 ppb, 500 ppb, and 1 ppm (dashed line) concentrations of H_2S gas.

3.5. PANI based hydrochloric acid sensors

Hydrochloric acid (HCl) is very dangerous for both humans and the environment. Exposure to concentrated HCl may cause circulatory collapse or asphyxia, while exposure to low concentrations solutions may lead to many health problems ranging from conjunctivitis to pulmonary oedema. As the airborne acceptable exposure limit for HCl in 8 h work day is 5 ppm, there is definite need for developing HCl sensors. [2] Nanocomposites of polyaniline and formaldehyde copolymer with a metal complex of Fe-Al obtained using thermal vacuum evaporation deposition techniques proved to be selective, fast and sensitive HCl gas sensor, which detects HCl (0.2-20 ppm) in 8-10 s and works at room temperature [49].

3.6. PANI based carbon oxides sensors

The main carbon oxides are the monoxide and the dioxide. The first is a hazardous and poisonous gas with a PEL (Permissible Exposure Limit) of 35 ppm (10-h ceiling limit) [50], while the latter is the main greenhouse gas responsible of global warming and atmosphere change, with exposure limits of 10,000 ppm (8-h Time-weighted average), and therefore there is a important need for developing sensors that can detect them.

A chemiresistive gas sensor based on polyaniline (PANI) nanofibers for CO detection was produced by a template-free electrochemical polymerization of aniline on an interdigitated electrode, a process that leads to the formation of a horizontally oriented, monolayered PANI nanofiber network. The nanosensor had an excellent responding ability on CO with a concentration as low as 1 ppm. The responding mechanism was credited to the different binding sites of CO and H_2 with PANI: the first with the unprotonated amine nitrogen atoms and the latter with the protonated amine nitrogen atoms [51]. PANI/Co_3O_4 nanocomposite sensors proved to be highly selective to CO at room temperature, with a high response of 0.81 obtained for 75 ppm CO concentration and a response time of 40 s [52].

Sensors made by vacuum-deposited PANI-Fe:Al (80:20) nanocomposite thin films produced rapid and selective detection of CO in the range 0.006-0.3 ppm at room temperature, with high sensitivity of the order of 400-600, and response times of 10 s [53] .

Sulphonated polyaniline (SPAN) was tested for sensing carbon dioxide at room temperature, showing significant conductivity change below pH 7. The impedance of SPAN films decrease when exposed to CO_2 concentrations higher then 20,000 ppm. To increase the sensor sensitivity for CO_2 SPAN was blended with polyvinyl alcohol [54]. A PANI/TiO_2 nanocomposite thin film based chemiresistive sensor developed a response for 1000 ppm CO_2 concentration of 5% at 35^{o}C. The response was 1% with increasing temperature to 60^{o}C. The response and recovery time characteristics of the sensor were found to be 70 s and 80 s, respectively [55].

A CO_2 room temperature gas sensor was produced using thick films of chemically synthesized cerium (Ce) doped PANI screen-printed on a glass substrate. It was found that the response decreased with an increase in the molar concentration of CeO_2, while the resistance of all Ce-doped PANI films increased with an increase in CO_2 gas concentration, supposedly because O^-_2 ions form weak bonds with π-electron clouds of PANI removing electrons from the bulk, subsequently increasing the barrier height and the resistivity [56].

3.7. PANI based sulphur dioxide sensors

Sulphur dioxide (SO_2) is a poisonous gas that affects the respiratory system; the exposure limit for SO_2 is of 5 ppm [57]. Consequently, its monitoring is much needed. Films of polyaniline doped with HCl and CSA have been used for SO_2–N_2 mixtures detecting. It was found that the electrical conductivity of PANI/HCl films is greater than that of PANI/CSA films due to the more closely packed crystalline domain which reflects its greater charge carrier mobility. The lowest detectable concentration is 200 ppm and the responses to SO_2 are reversible [58].

A polyaniline–tungsten oxide hybrid nanocomposite was used for sulphur dioxide monitoring at room temperature. The sensing response of the sensor is significantly bigger as compared to that of polyaniline nanofibres for 10 ppm SO_2 at room temperature, and the reason for this behaviour might the better porosity, the branched structure and the formation of heterojunctions. [59].

4. Polyaniline as sensor for volatile organic compounds (VOCs)

Volatile organic compounds are organic substances that have a high vapour pressure at room temperature, such as benzene, formaldehyde, methylene chloride, perchloroethylene and many others. Many of the VOCs endanger human health as well as the environment and contribute to climate change and destruction of the ozone layer [60]

Formaldehyde, which is used in many manufactured products, is one of the more toxic volatile organic compounds [61]. A sensor fabricated by using PANI intercalated MoO_3 thin films, (PANI) x MoO_3, on $LaAlO_3$ substrate exhibits distinct sensitivity to formaldehyde (HCHO) and acetaldehyde (CH_3CHO) vapours [62] PANI nanofibre based sensors (d = 300 nm) detect hydrazine which rapidly reacts with the emeraldine base and converts it to leucoemeraldină, a process influenced by humidity [41] and temperature [63]. This is why these variables have to be maintained constant (laboratory experiments) or there influence has to be compensated (operating devices).

Chloroform vapours can affect the central nervous system and damage the liver and kidneys, and this is why the recommended exposure limit is of only 2 ppm (for 60 min) [64]. A copper/PANI proved to be effective for $CHCl_3$ detection in the range of 10-100 ppm, with sensitivity values varying in the range of 1.5-3.5 [65]. A PANI/Pd nanocomposite was used for sensing methanol, a widely used substance that is flammable, explosive and toxic to human beings even in small concentrations. The short-term exposure limit for methanol is of 800 ppm. The sensors revealed a high response for 2000 ppm methanol. [66] PANI doped with camphor sulfonic acid presented a good response to alcohol vapours by undergoing a change in the electrical resistance, which decreases in the presence of small chain alcohols but increases in the case of long chain alcohols [67].

A polyaniline (PANI)/SnO_2 hybrid material was employed for sensing ethanol and acetone. The sensor is ineffective to ethanol and acetone at 30°C, but it becomes sensitive to these vapours when operated at 60 and 90°C, with an acceptable recovery time [68].

5. PANI sensors for liquefied petroleum gas (LPG)

LPG is highly inflammable and consequently its detection at room temperature is crucial. PANI based nanocomposite proved to be efficient for LPG sensing at room temperature, with excellent stability and short response and recovery times [69]. A PANI/g-Fe_2O_3 nanocomposite sensor was used for detecting LPG room temperature, exhibiting a response of 1.3 for 200 ppm LPG. The mechanism for the detection of LPG is suggested to be the result of an increase in the depletion depth due to the adsorption of gas molecules at the depletion region of the p-n heterojunction [70].

A sensitive and selective LPG sensor was fabrication based on electrospun nanofibers of PANI/ZnO nanocomposites [71]. The sensitivity of the sensor increases from 1.11% to 7.33% at 36°C, but at further increase in temperature from 36°C to 90°C the sensitivity decreased to 1.25%. Polyaniline/Barium zirconate ($BaZrO_3$) composites have been used for LPG sensing. The LPG sensitivity of about 1% at 40,000 ppm was obtained for 50 wt% $BaZrO_3$ in PANI [72-74]. A PANI/Cu_2ZnSnS_4 thin film based heterostructure was used for detecting LPG at room temperature. The maximum gas response of 44% was obtained at 0.06 vol% of LPG, but the LPG response decreased to 12% at the relative humidity of 90%. The PANI/CZTS heterojunction showed good stability and fast response and recovery time periods [74-76].

6. Conclusions

Polyaniline, alone or associated with different polymers or mineral substances, has many applications as gas sensor, due to its capacity to convert a chemical interaction (a variation in its protonation or oxidation state) into an electrical signal. Polyaniline based sensors are effective at room temperature in detecting many mineral or organic hazardous substances, showing good selectivity and stability and fast response and recovery time. This review analyses the most recent progresses in the field of PANI hybrid nanocomposites for gas/vapour sensors, pointing up their huge versatility and highlighting the most important features and possibilities for further development.

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