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Conducting polymer and metal-based sensors for the detection of vapours and toxic gases: A concise review

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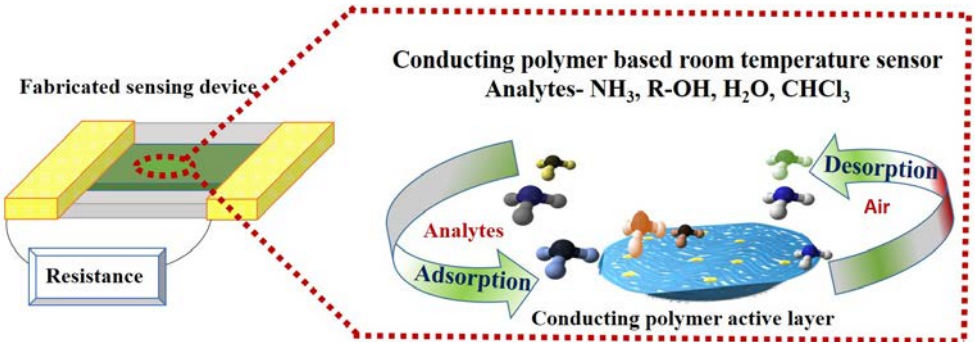
Review

ABSTRACT



Monitoring the concentration of gases and volatile compounds in the environment has significant impact on sustainable human development due to global industrialization. Gas sensors are being employed since 1970's for detecting noxious gases, gas leakages, and also for observing humidity and atmospheric composition. The approach of designing miniature and portable gas/vapour sensors exhibiting rapid response and reversibility together with selectivity and sensitivity has been highly demanding. Similarly, development in the area of nanotechnology has encouraged the scientists to fabricate nanosensors. Sensor devices have been made from classical semiconductors, solid electrolytes, insulators, metals etc. However, the development of conducting polymer-based sensors has unfolded a new dimension in sensing by enabling the wide scope towards the detection of chemical/water vapours and toxic gases even in complex environment. Whereas, the metal oxide-based sensors were observed to be efficient towards the detection of toxic gases. The present review provides a concise account of our work on conducting polymers and metal-based sensors for the detection of ammonia, alcohol, chloroform, humidity, toxic gases etc. Additionally, the paper also demonstrates the challenges and future prospects of conducting polymer sensors to pave their way for enhancing their sensing efficacy.

Keywords: Room temperature sensor, polyaniline, substituted polyanilines, metal doped-polyaniline, chemical vapors, gases

INTRODUCTION

Over the past few decades, advancement in the technologies and industries have resulted into the proliferation of a pool of harmful gases and vapours in the environment, mostly detectable only at high concentrations.[1] On the other hand, detection of the low concentration of such noxious gases has been challenging and imperative. The real-time detection of toxic compounds and volatile contaminants has been envisaged to minimize the ensuing environmental hazards.[2] Therefore, it demands the development of highly sensitive, fast, and selective sensors that can operate under ambient conditions.

Until recent years, enormous gas sensing strategies have evolved, however, the metal oxide-based sensors have been considered as the most popular owing to their ease of fabrication and the scope for miniaturization.[3,4] In 1962, Seyama *et al.* demonstrated the very first commercial gas sensor using ZnO thin films operating at 480°C.[5] Further, the arena of semiconductor gas sensors has expanded substantially to improve their selectivity, sensitivity and fast response. Despite significant advancement in the material science, high operating temperature with higher power consumption of these thermally activated semiconductor metal oxide based sensors has limited their applications.[6] Hence, researchers were mainly focused on modifying them to lower their operating temperatures by relying

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significantly on nanotechnology. Several approaches such as surface deposition using noble metals, porous nanostructures, 2D nanostructures further opened various avenues to optimize the material parameters.[7–10]

The quest towards developing economical room temperature sensors has led to the utilization of conducting polymers.[11–14] Among the family of conducting polymers, the investigations on conducting polyaniline (PANI) have played a vital role in developing real time sensors in addition to their simplicity, rapid response as well as cost-effectiveness.[15–18] Besides, various parameters such as electrical conductivity, proton doping, secondary dopants and redox switch over properties govern the overall facile charge transport and their sensing capabilities. Additionally, by virtue of nanotechnology, numerous nanostructures of conducting PANI were synthesized by using an array of synthetic modes or by incorporating nanoparticles during polymerization, however, achieving superior selectivity towards specific analytes beyond the existing state-of-the-art materials remained as a monumental task.[19,20] Conventionally, nanoparticles of metals, metal oxides, and carbonaceous compounds have been incorporated in conducting polymers owing to their synergistic properties.[21] Besides, the augmented physicochemical properties, the conductivity and conductive pathway of polymers in the nanocomposite result in the enhanced sensitivity of the nanocomposite towards the target analytes.

It is worth noting that, optimizing the concomitant surface attributes (dimensionality) of the sensor active layer indeed plays a critical role in achieving efficient sensing performance.[22] In the context of alcohol vapours sensing, rapid evolution in device fabrication has been accomplished by using a multidisciplinary approach. Methanol is often used as a solvent or chemical feedstock in laboratories and chemical plants, posing a possible hazard of intoxication. Nanostructured metal-oxide sensors are investigated for fast response of methanol up to 5 ppb, however, such sensors are non-selective representing a long-standing challenge.[23] Engineering control over the desired structure of metal oxide and designing sensor is highly critical to ensure both, sensitivity as well as selectivity.[24] Similarly, ethanol is also widely used in various industries like food, beverage and also as a solvent, is toxic more than its permissible limit.[25] Considering circumstances mentioned above, achieving selectivity towards a specific alcohol is one of the extensively investigated areas and it is worth mentioning that metal/metal oxide inclusions into PANI matrix could pave the way with a great efficacy.[26]

Ammonia (NH_3) is reported as the second largest chemical globally in its industrial production and are consumed in various fields such as agriculture, hydrogen fuels, automotive, defence, medical diagnostics, and food processing. Though the presence of ammonia in nature is very trace amount (upto ppb level), its control and real-time monitoring hold significance since its long term exposure of more than ~25 ppm cause pulmonary diseases.[27–29] Appropriate modification of conducting polymer - based sensors are promising in terms of flexibility as well as performance.[30,31]

The term “humidity” is commonly used to quantify the amount of water vapours in the gas or atmosphere. Since water vapours play a significant role in sustaining quality and efficacy for products and technologies that are used every day as well as being essential for human existence. Hence, accurate measurement and controlling humidity are vital in various fields to prevent the damage and deterioration of air-conditioning systems, electronic devices, food etc.[32,33] Conducting polymers have been extensively investigated in this regard and the challenges associated with such materials can be addressed by optimization of dopant acid, doping level or blending with other polymer/ metals etc.[34]

Unlike the aforementioned analytes, detection of hazardous vapours such as chloroform has always been challenging due to its inevitable disposal into the atmosphere by various anthropogenic activities.[35] It is considered as one of the major concerns since it possesses high solubility in water at room temperature (~25 ^oC), can easily result in groundwater pollution also leads to serious deteriorating effects to human health.[36] Therefore, accurate monitoring is essential, but is highly challenging since most of the sensors are very susceptible to many environmental factors such as temperature, humidity, etc.[37]

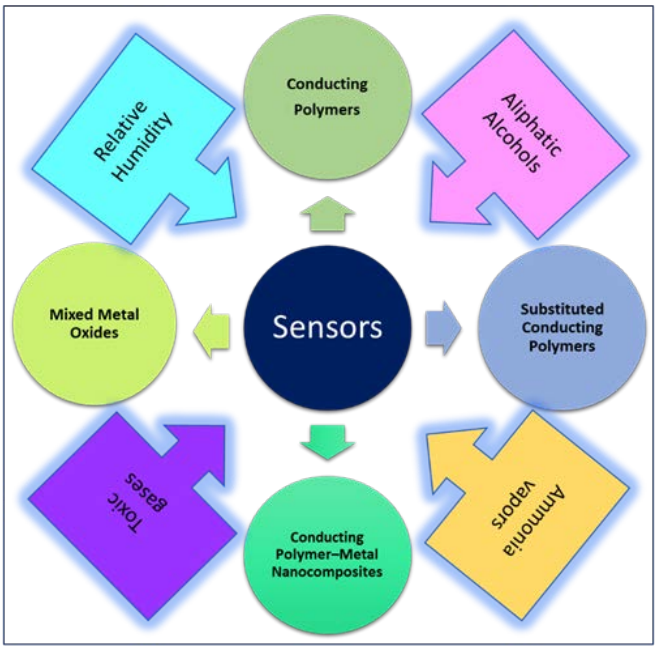

Figure 1. A typical schematic diagram representing the overview of various sensing materials and analytes investigated.

The detection of various noxious gases such as nitric oxide (NO), carbon monoxide (CO), are of vital importance due to their enormous physiological impact. Perovskite materials were found to be potential candidates for sensing gases however, the structural and morphological intricacies dictate their sensing mechanism.[38,39] Due to the presence of a large number of oxygen vacancies or deficiency sites on the surface, metal oxide perovskites are recognized as sensing materials.[40] Here, the primary difficulty lies in obtaining a suitable phase, predominantly comprising active sites for adsorption of specific analyte (gas). Hence, a careful synthetic strategy of perovskite

materials would pave the way to afford explicit sensing behaviour.

The primary objective of the current review is to demonstrate the efficacy of conducting polymers and metal-doped conducting polymers as room temperature sensors for chemical vapours/toxic gases, work carried out over a couple of years and published earlier by our research group.[41–48] The major contribution of this review includes the study of pristine polyaniline (PANI), substituted derivatives of PANI, and metal decorated PANI composites for sensing chemical vapours/gases. Various analytes investigated were a series of aliphatic alcohols, chloroform, ammonia and humidity. Further, an effort was made to develop perovskite materials by varying morphology for sensing CO and NO gases.[49] Thus, the concise review on room temperature sensors is devoted to highlighting several approaches with an intention to encourage the researchers for opening various avenues to envisage futuristic devices. Figure 1 provides an overview of the various sensing materials and analytes mentioned in this review.

Role of Conducting Polyaniline and Metal doped Polyaniline nanocomposites for Room Temperature Sensing

Influence of mode of synthesis and selection of dopants on sensing properties

The mode of synthesis and parameters of polymerization plays a pivotal role as they impinge upon the resulting conducting polymers in terms of electrical conductivity, morphology and consequently their sensing applications.[50] Designing nanostructured materials have also been significantly investigated over decades to achieve long term stability, rapid response, enhanced sensitivity, high selectivity and reproducibility. Another key factor affecting the sensing properties of conducting polymer is the surface interaction with analytes. Li *et al*. has demonstrated a convenient method for progressively modifying the morphology of PANI from nanofibers to films by varying the ratio of solvent composition of the casting solution.[51] The authors reported that, although PANI nanofibers with the superior surface area were fast in response, the lower sensitivity was ascribed to the enhanced contact resistance. Hence, augmenting surface area merely cannot contribute to superior sensing performance. The strategy of binary dopant acid has also been a potential methodology for modifying the desirable characteristics by enhancing the figure of merits of adsorption.[52] Besides, inclusion of various metals/ metal oxide offers a multifunctional approach wherein, a secondary component not only varies the morphology but also enhances electronic interaction along with many other novel features.[21,53]

Various strategies have been adopted for incorporating nanoparticles in the PANI matrix. Cho *et al* and Bedre *et al* have reported interfacial polymerization to obtain Pt and Ag-doped PANI respectively.[54,55] An effective electrochemical strategy of metal doping was explored by Kinyanjui *et al*.[56] However, *in-situ* polymerization is a commonly employed method as it provides better control over the size and shape.[57]

Conducting polymers based room temperature sensors

In this section, the authors have highlighted the sensing behaviors of bare/ substituted PANI towards different analytes. In one of the earlier reports, pristine polyaniline and its substituted derivatives (poly o-toluidine, poly o-anisidine, poly N-methyl aniline, poly N-ethyl aniline, poly (2,3 dimethylaniline), poly (2,5 dimethylaniline) and poly diphenyl amine were tested for their sensing ability towards saturated

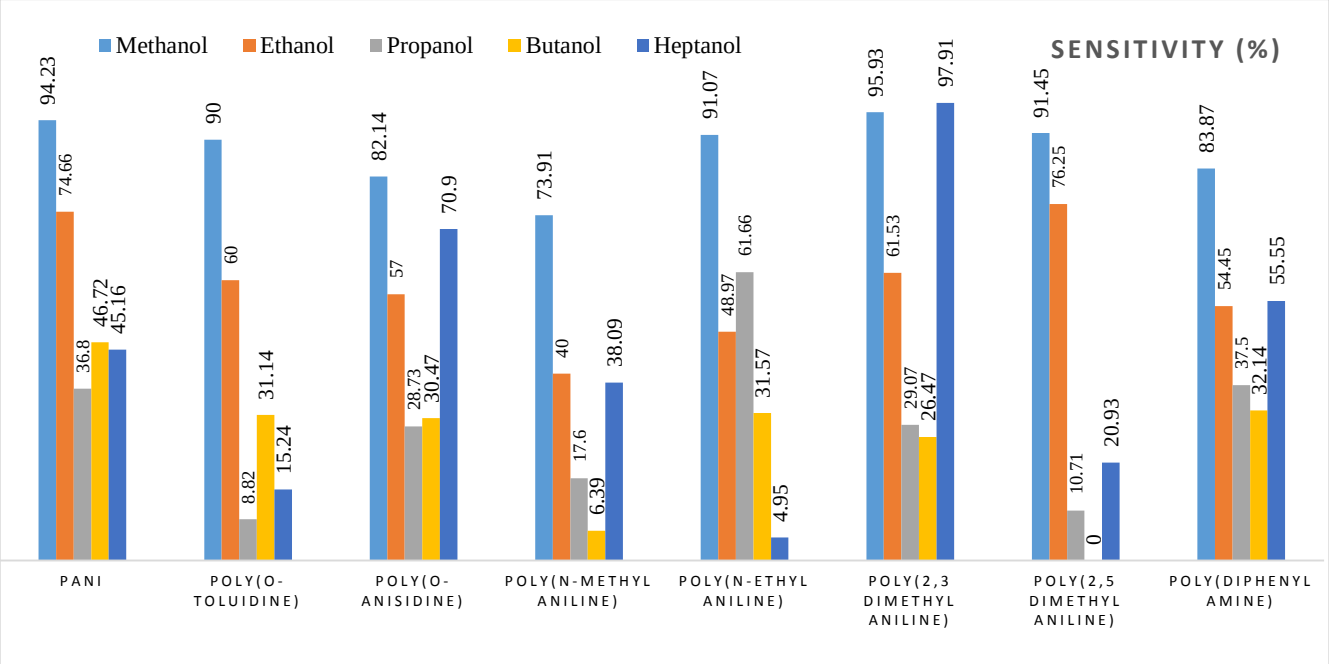

Figure 2. Sensitivity (%) of polyaniline and substituted derivatives towards different alcohol vapours.

vapours of a series of aliphatic alcohols such as methanol, ethanol, propanol, butanol and heptanol.[42] The polymers were synthesized by the chemical oxidation method using HCl as the dopant in presence of an oxidizing agent, ammonium persulphate. All the polymers were responding to different analytes as a function of concentration, while the difference in the sensing behaviour was observed to be distinct in terms of rapidity, reproducibility and sensitivity. Figure 2 displays the sensitivity of polyaniline and its substituted derivatives towards various analytes.

The trend in resistance showed a negative paradigm in presence of small chain alcohols viz. methanol, ethanol and propanol, conversely, a reverse trend was noted when subjected to higher homologues (butanol and heptanol vapours). This difference has been attributed to the size of the molecules, methanol molecules being small in size can interact and diffuse most efficiently in the polymeric matrix compared to the higher homologues. Secondly, due to high polarity, methanol molecules interact strongly with the imine nitrogens leading to the uncoiling of the polymeric chains and consequently the crystallinity [Figure 3].[58,59] On the other hand, butanol and heptanol molecules being large in size, only a few molecules of butanol and heptanol could diffuse efficiently into the polymeric matrix for identical exposure time as that for methanol and therefore did not impact on crystallinity [Figure 3C]. The lowest measurable response was exhibited for a concentration upto 3000 ppm of alcohol. Both poly (2,3-dimethylaniline) and PANI exhibited rapid response towards methanol and ethanol, however, the highest sensitivity i.e., more than 80% was merely observed for only methanol.

Also, chemically synthesized polyaniline and its ring substituted derivatives such as poly(o-toluidine), poly (2,3 dimethylaniline) and poly (2,5 dimethylaniline) were utilized as sensors for relative humidity (RH 6.4-97.3%) to test the water poisoning effect on the same.[43] The conductivity of all the sensors showed a decrease at all RH concentrations except at 97.3 % RH where it was observed to increase. The varying trend was attributed to the polymeric backbone with the ingress of water. At lower percent humidity, the mobility of the dopant ion was restricted due to the inherent coiled structure of the polymeric chains while, on hydration, the conductivity was augmented due to the uncurling of the compact-coil as a result of secondary doping effect of water molecules.

The interaction of polymeric backbone with water was justified by the FTIR analysis [Figure 4].

The increase in the intensity of peak at ~3200 cm^{-1} corresponding to -N-H stretching vibrations together with the shift to ~3171 cm^{-1} accounts for the transition from unprotonated (non-conducting) form to protonated form (conducting form) at a high percentage of relative humidity. A comparative study revealed that, among all, poly (2,3-dimethylaniline) exhibited higher sensitivity [Figure 5], as well as linear response was concluded as a competent material for a potentially viable humidity sensor.

Further, to explore the evident effect of dopant acids, acrylic acid (AA-PANI) and HCl doped polyaniline (HCl-PANI) were also studied for sensing ammonia vapours.[44]

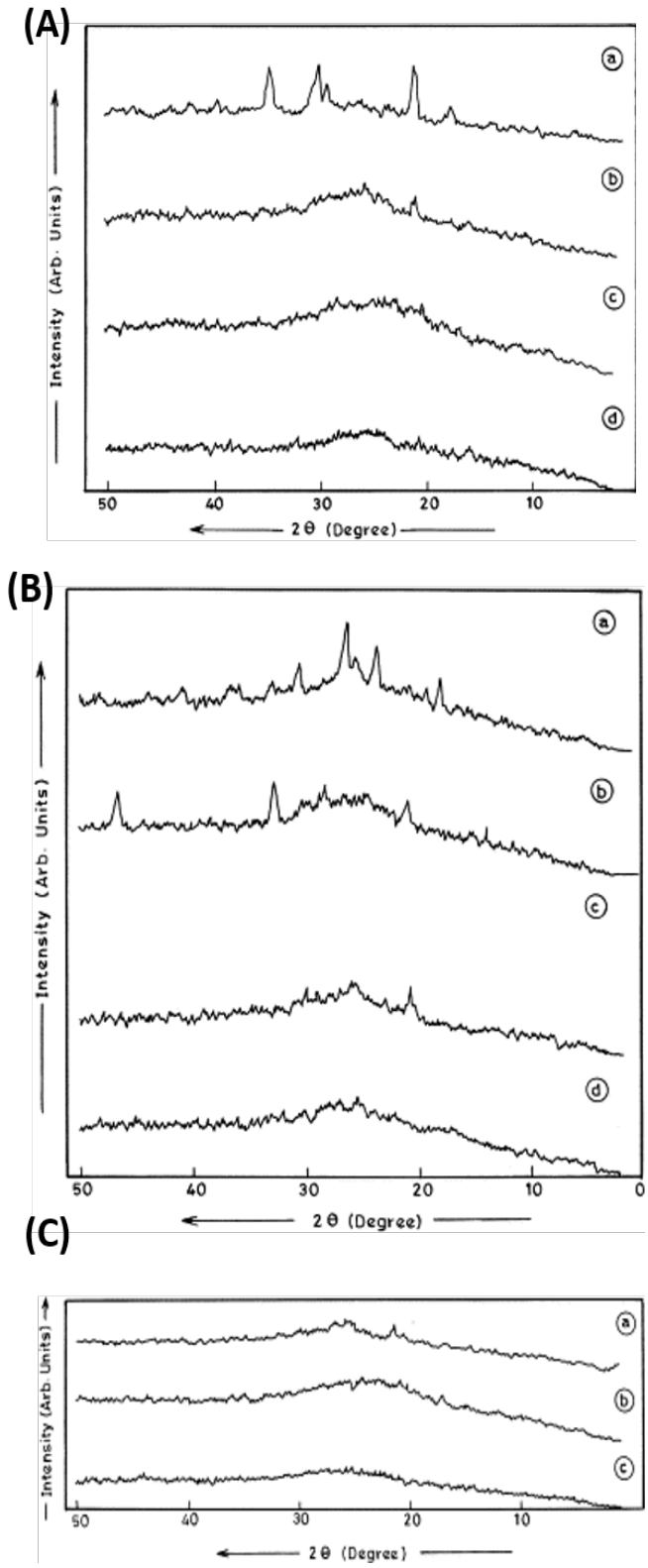

Figure 3. Wide angle X-ray diffraction patterns of (a) polyaniline (b) poly o-toluidine (c) poly N-methylaniline and (d) poly (2,3 dimethylaniline) (A, B) before and after exposure to saturated methanol; (C) After exposure to heptanol (a) polyaniline (b) poly N-methylaniline and (c) poly (2,3 dimethylaniline). Reprinted with permission from Ref. [42], Copyright 2000, Elsevier.

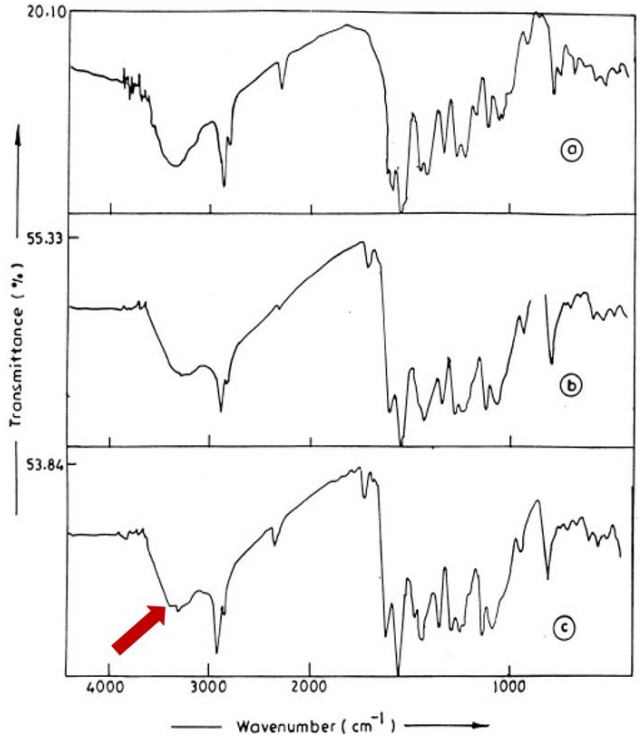

Figure 4. FTIR spectra of poly (2, 3 dimethylaniline) (a) before exposure (b) exposure to 6.4% RH, and (c) exposed to 97.3% RH. Reprinted with permission from Ref. [43], Copyright 2001, John Wiley & Sons.

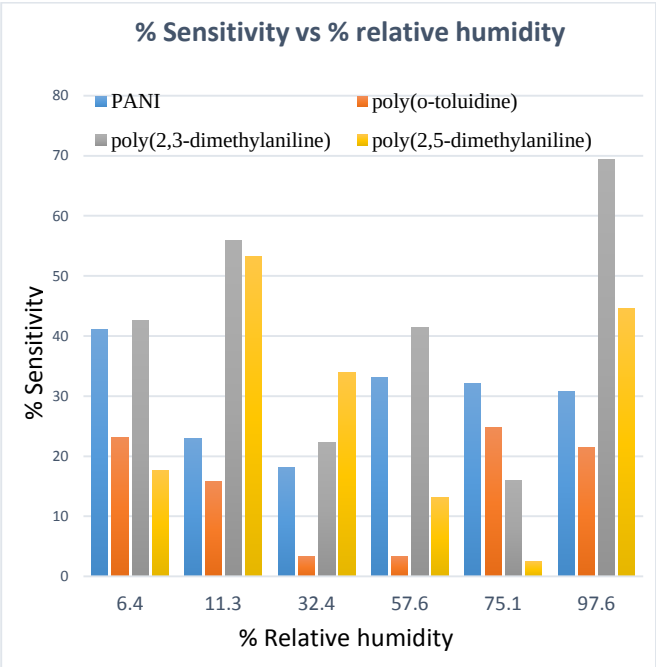

Figure 5. Sensitivity (%) of polyaniline and its substituted derivatives towards relative humidity.

A comparison of responses revealed that on exposure to ammonia, the former material exhibited higher sensitivity and reversibility in terms of decrease in resistance, whereas an opposite trend was noted in the latter case. A decrease in conductivity for HCl-PANI has been attributed to the conversion of conducting emeraldine salt phase into the non-conducting emeraldine base arising due to interactions between ammonia and HCl dopant. The opposite trend in response values (10^2 kΩ) in the case of AA-PANI samples on exposure to ammonia in contrast with the conventional dopants further prompted the authors to investigate the same.[45] In addition to the secondary doping effect of acrylic acid, an additional site (COO^-) free for conduction was induced while reacting with ammonia in the polymeric chains and consequently the conductivity.[60,61] The sensitivity of AA-PANI samples was studied over a wide range of concentrations of ammonia vapours from 1 to 600 ppm. The ΔR/R showed a linear increase up to a concentration of 58 ppm followed by saturation [Figure 6A].

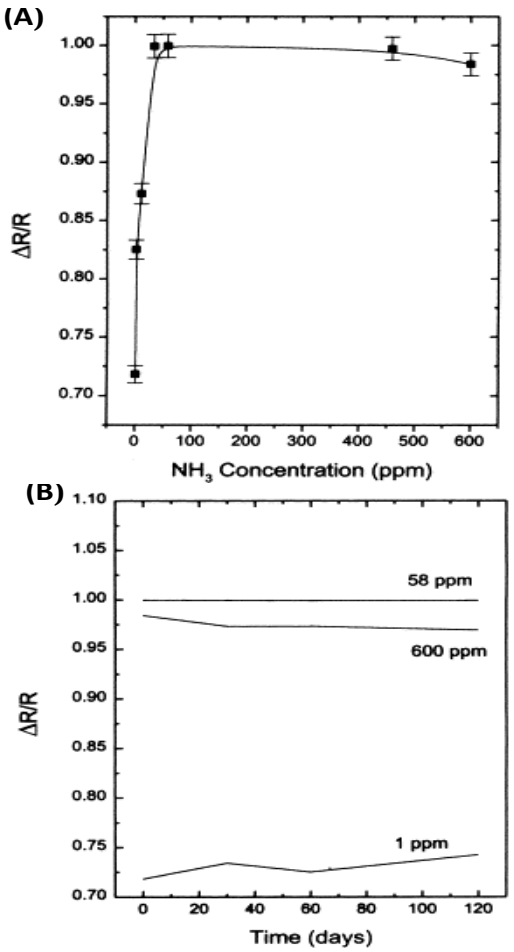

Figure 6. Variation of Δ*R*/*R* of acrylic acid doped polyaniline A) Exposed to ammonia B) Long-term stability of acrylic acid doped polyaniline sensor. Reprinted with permission from Ref. [45], Copyright 2001, Elsevier.

It should be noted that the sensor exhibited high sensitivity even at a concentration of 1 ppm at room temperature and was chemically stable upto 120 days [Figure 6B]. These results reiterate their employability as state-of-the-art materials. A typical mechanism of interaction of ammonia with PANI while sensing is represented in Figure 7.

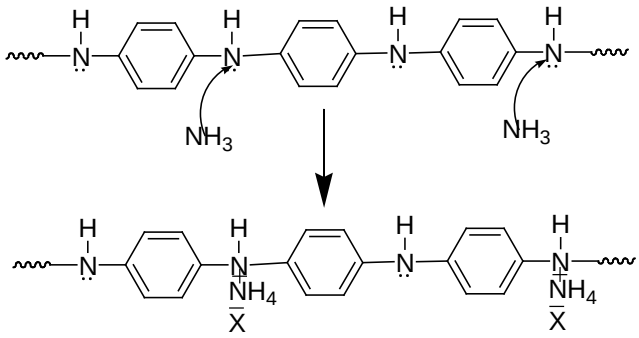

Figure 7. Mechanism of PANI-ammonia interactions.

Metal-conducting polymer nanocomposites as room temperature sensors

With the advent of nanotechnology, a thought provoked us to extend our work to explore the applicability of nanocomposites of conducting polymers that could be useful in developing nanosensors. As from the earlier studies, the sensing mechanism was observed to be an adsorption/desorption process and metal surfaces are known for their catalytic performance, nanocomposites of PANI were prepared by dispersing nanoparticles of Pd, Ag and Cu metals etc.[62] The sensitivity and selectivity of nanocomposites of metal based polyaniline sensors were observed to be strongly dependent on the type of metal present. Besides the synergistic approach, metal acts as a secondary dopant at the nitrogen site of the PANI quinoid units and creates an active site when exposed to various analytes [Figure 8].

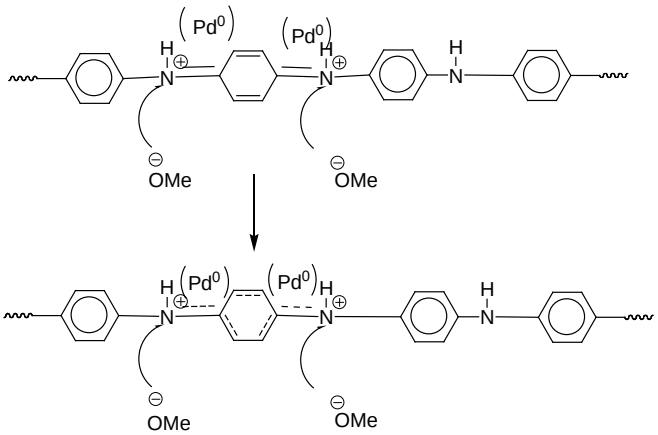

Figure 8. Mechanism of the Pd doped PANI nanocomposite-alcohol interactions.

In early 2002, the considerable demand for an economical, portable real-time monitoring device had triggered our research group to investigate the applicability of PANI as a matrix for Cu nanoclusters for the detection of chloroform by measuring its increased resistance.[41] The predominant role of Cu nanoclusters was evident from the remarkable difference in the response behaviour of pure PANI and Cu-PANI nanocomposites. The enhancement in adsorption–desorption of chloroform vapours assured superior interaction of the active sites provided by Cu nanoclusters. The response of Cu-PANI towards chloroform vapours was reproducible and superior for concentrations below 100 ppm.

In a typical procedure, silver nanoparticles were prepared by the γ-irradiation method using different concentrations of aniline (0.05-1.0 M) as a stabilizer in a 1:1 methanol-water mixture.[46] The silver particles displaying stability upto a period of 7 days were obtained in presence of 0.1M aniline. The stable silver-aniline was further oxidized by the dropwise addition of ammonium persulphate at 5 ^{o}C for 2 h under constant stirring. These nanocomposites exhibited highly sensitive and reproducible responses towards ammonia vapours involving change in the resistance of the order 10^2 (hundreds).[47] The response towards ammonia was consistent up to 20 cycles. The study revealed that the reduction in grain size is one of the key attributes augmenting the sensing characteristics in the case of nanocomposites.

Table 1: A comparative performance of metal-polymer nanocomposite sensors towards respective analytes

Active material	Analyte	Concentration of analyte	Sensitivity (Ω ppm^{-1})	Ref
Ag-PANI	Ammonia		6.6 x 10^5	47
Ag-PANI	Ethanol	100 ppm		63
Ag-PANI	Ethanol	500 ppm		64
Pd-PANI	Methanol	--	8.9 x10^5	48
Pd-PANI	Methanol	--	8.9 x 10^4	65
Pd-PANI	Ammonia	500 ppm	--	66
Au-PANI	Hydrogen sulphide	0.1 ppb	--	67
Au-PANI	Ammonia	100 ppm	--	68
Co-PANI	Water	----	8 s with recovery time of 1 min	69

In continuation of the work on metal-PANI nanocomposites, the potential of Pd-polyaniline sensors was explored.[48] The nanocomposite was prepared by a two-step method, wherein Pd nanoparticles were synthesized by the reflux method followed by chemical oxidative polymerization of Pd nanoparticles-aniline mixture. The designed sensors were exposed to various aliphatic alcohol vapours such as methanol, ethanol, and isopropanol, however, the Pd/PANI sensors responded rapidly and reversibly towards methanol vapours. The selectivity of the nanocomposites was demonstrated by exposing the composite to the mixture of methanol +ethanol (1500ppm, 700 ppm) methanol+ isopropanol (1500 ppm, 900 ppm) vapours. The degree of response of the sensor was found to be similar to that of pure methanol, however, the time of response was observed to be increasing from 2s to 12 min for the corresponding mixtures. A plausible mechanism justified the selectivity and the increase in the time of response owing to the higher polarity of methanol and the competition

between adsorption-desorption of the different alcohol molecules present in the mixture. The response curve of PANI and Pd doped PANI towards various concentrations of methanol is displayed in Figure 9.

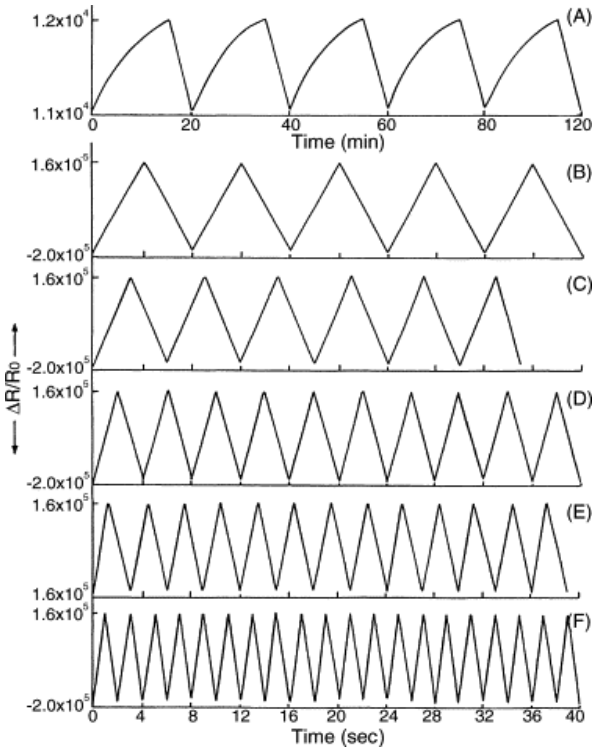

Figure 9. Response curves of (A) blank PANI exposed to saturated vapours of methanol (2000 ppm) and Pd–PANI nanocomposite exposed to methanol concentrations of (B) 1 ppm; (C) 5 ppm; (D) 10 ppm; (E) 100 ppm; and (F) 2000 ppm. Reprinted with permission from Ref. [48], Copyright 2006, Elsevier.

From our aforementioned studies, it was evident that the mode of synthesis of metal and metal incorporated nanocomposites had played a key role in dictating the sensing behaviour. To strengthen the claim, nanocomposites of Pd-PANI synthesized by thermal reduction (reflux) and γ radiolysis methods were investigated.[65] Both the nanocomposites were exposed to different alcohols and their response time revealed an unambiguous sensitivity towards methanol vapours. Furthermore, the selectivity was also investigated using methanol as well as mixtures of various alcohols (methanol-ethanol and methanol-isopropanol). Both the nanocomposites rendered identical responses towards methanol and the mixture containing methanol, however, there was a remarkable difference witnessed in the magnitude as well as the time of response of the individual nanocomposites. The obtained results displayed the superior sensing performance for Pd-PANI nanocomposite synthesized by the thermal reduction method when compared to γ radiolysis. This has been credited to the uniform particle size of the Pd nanoparticles synthesized by the thermal reduction method facilitating the rapid adsorption-desorption of methanol vapours over the nanocomposite. The difference in polydispersity of Pd nanoparticles due to the difference in synthesis are schematically represented in Figure 10.

Further, Table 1 compares the performance of various metal-polymer nanocomposite sensors towards respective analytes.

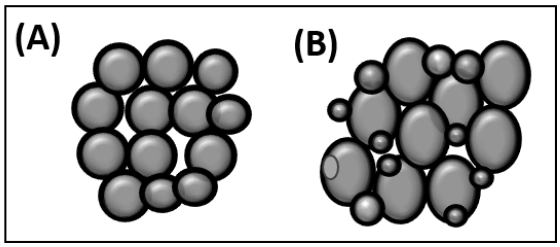

Figure 10. Pd nanoparticles synthesized by A) reflux method with low dispersity and (B) irradiation method with higher poly dispersity.

Mixed metal oxide as gas sensors

Ruddlesden–Popper (RP) oxide (A_2BO_4) structures are layered perovskites consisting of alternate layers of ABO_3 and A-O rock salt where A and B are cations of metals and O is oxygen. They are reported to be promising for high temperature sensing applications.[70] Among all, Lanthanum cuprate (La_2CuO_4) has been explored for its sensing ability as it displays unique properties owing to its oxygen deficiency.[49]

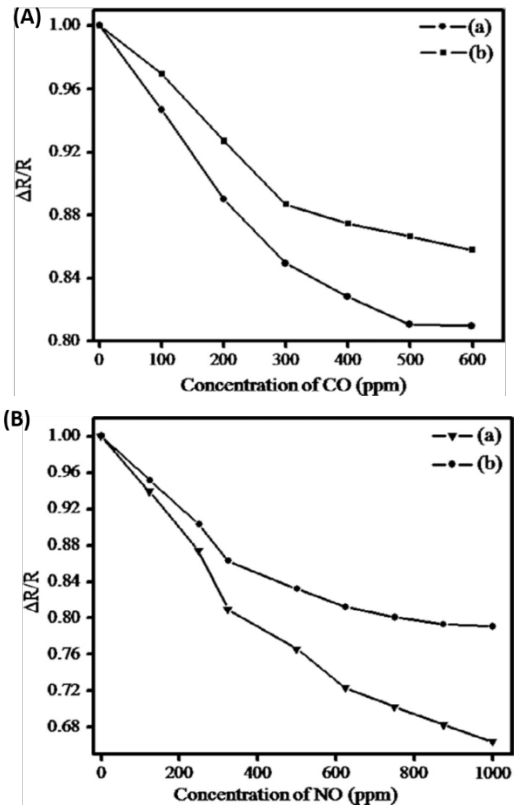

Figure 11. Gas sensor responses of the La_2CuO_4 synthesized with (a) acetate and (b) nitrate precursors for A) CO and B) NO. Reprinted with permission from Ref. [49], Copyright 2014, Elsevier.

The study has emphasized the role of various precursor salts (nitrate, chloride and acetate) and its molar ratio which governs

the oxygen vacancies in the lattice and thereby the sensing process. Figure 11 displays the response behaviour of La_2CuO_4 synthesized with (a) acetate and (b) nitrate precursors towards CO and NO gases respectively. The template-free approach of the aforementioned materials exhibited a positive response towards low temperature sensing of CO (1 ppm to 600 ppm) and NO gas (1-1000 ppm) at 350 ^oC and 250 ^oC respectively. The studies could reveal that the sensor response showed a sharp decrease upto a concentration of 300 ppm of CO followed by a change in slope at a higher concentration of analyte reaching saturation, whereas the same was observed to be upto 250 ppm in case of NO detection. The sensing behaviour was found to be very similar to n-type materials with the decrease in resistance in presence of reducing gases.[71] A plausible mechanism has been postulated demonstrating the adsorption of oxygen on the sensor surface and interaction with electrons. Recently, Hu *et al.* attempted to improve the non-stoichiometric oxygen deficiency by doping with Bismuth and Strontium, a highly promising approach that could be further explored towards gas sensing.[72]

Conclusions and Future Prospects

In this section, an overview of room temperature sensors and highlights of our research work are given. It would further shed light on the current research on similar materials to overcome the shortcomings. The major conclusions are as follows:

- Room temperature sensing of PANI, substituted PANI and metal-PANI nanocomposite towards alcohol, ammonia, chloroform and ammonia are discussed.
- The influence of microstructural parameters on the rate of adsorption and desorption of analyte molecules.
- The effect of interaction of analytes and sensing materials on both sensitivity and selectivity.
- The effect of mode of synthesis and incorporation of nanostructures on adsorption–desorption mechanism during the gas–solid interaction.

There are numerous vital issues that need to be resolved in future for product development. Fabrication of sensors with increased sensitivity and accuracy even at trace level detection is going to be the line of research in coming days. Research based on miniaturization of sensors using polymer based electrodes has been a point of attraction of various industries. The role of controlled growth of grains, grain boundaries, and nanostructured morphologies narrated in many available reports underlying mechanisms still require in-depth investigations with respect to theoretical concepts.

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Conflict of Interest

Authors declared no conflict of interest.

References and Notes

1. X. Cong. Air pollution from industrial waste gas emissions is associated with cancer incidences in Shanghai, China. *Environ. Sci. Pollut. Res.* **2018**, 25 (13), 13067–13078.
2. N. Joshi, T. Hayasaka, Y. Liu, et al. A review on chemiresistive room temperature gas sensors based on metal oxide nanostructures, graphene and 2D transition metal dichalcogenides. *Microchim. Acta* **2018**, 185 (4), 213.
3. J. Zhang, Z. Qin, D. Zeng, C. Xie. Metal-oxide-semiconductor based gas sensors: screening, preparation, and integration. *Phys. Chem. Chem. Phys.* **2017**, 19 (9), 6313–6329.
4. V. Mounasamy, G.K. Mani, S. Madanagurusamy. Vanadium oxide nanostructures for chemiresistive gas and vapour sensing: a review on state of the art. *Microchimica Acta*. 2020.
5. T. Seiyama, A. Kato, K. Fujiishi, M. Nagatani. A New Detector for Gaseous Components Using Semiconductive Thin Films. *Anal. Chem.* **1962**, 34 (11), 1502–1503.
6. T. Gessner, K. Gottfried, R. Hoffmann, et al. Metal oxide gas sensor for high temperature application. *Microsyst. Technol.* **2000**, 6 (5), 169–174.
7. J. Zhang, X. Liu, G. Neri, N. Pinna. Nanostructured Materials for Room-Temperature Gas Sensors. *Adv. Mater.* **2016**, 28 (5), 795–831.
8. S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, A. Kis. 2D transition metal dichalcogenides. *Nat. Rev. Mater.* **2017**, 2 (8), 17033.
9. Y. Liu, X. Gao, F. Li, et al. Pt-In2O3 mesoporous nanofibers with enhanced gas sensing performance towards ppb-level NO2 at room temperature. *Sensors Actuators, B Chem.* **2018**, 260, 927–936.
10. S. Park, S. An, Y. Mun, C. Lee. UV-activated gas sensing properties of ZnS nanorods functionalized with Pd. *Curr. Appl. Phys.* **2014**, 14 (SUPPL. 1), S57–S62.
11. P.S. Barker, J.R. Chen, N.E. Agbor, et al. Vapour recognition using organic films and artificial neural networks. *Sensors Actuators B. Chem.* **1994**, 17 (2), 143–147.
12. K. Ogura, H. Shiigi, M. Nakayama, A. Fujii. Thermogravimetric/Mass and Infrared Spectroscopic Properties and Humidity Sensitivity of Polyaniline Derivatives/Polyvinyl Alcohol Composites. *J. Electrochem. Soc.* **1998**, 145 (10), 3351–3357.
13. A.G. MacDiarmid, W.J. Zhang, J. Feng, F. Huang, B.R. Hsieh. Thin films of electroactive oligomers and polymers: Application in sensors for volatile organic compounds and in light-emitting devices. In *Annual Technical Conference - ANTEC, Conference Proceedings*; **1998**; Vol. 2, pp 1330–1334.
14. G. Inzelt. Applications of Conducting Polymers. *Indian J. Chem. -Section A* **2012**, 245–293.
15. Y. Yan, G. Yang, J.L. Xu, et al. Conducting polymer-inorganic nanocomposite-based gas sensors: a review. *Science and Technology of Advanced Materials*. 2020, pp 768–786.
16. P.D. Virutkar, A.P. Mahajan, B.H. Meshram, S.B. Kondawar. Conductive polymer nanocomposite enzyme immobilized biosensor for pesticide detection. *J. Mater. Nanosci.* **2019**, 6 (1), 7–12.
17. S.B. Kondawar, A.M. More, H.J. Sharma, S.P. Dongre. Ag-SnO2/Polyaniline composite nanofibers for low operating temperature hydrogen gas sensor. *J. Mater. Nanosci.* **2017**, 4 (1), 13–18.
18. A. Dahiya, S.L. Goyal, D. Jain, N. Kishore. Synthesis and Fourier Transform Infra-Red Spectroscopy of Polyaniline/Cobalt Chloride Composites. *J. Integr. Sci. Technol.* **2017**, 5 (2), 47–49.
19. Y.Z. Long, M.M. Li, C. Gu, et al. Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers. *Progress in Polymer Science (Oxford)*. 2011, pp 1415–1442.
20. A. Rahy, D.J. Yang. Synthesis of highly conductive polyaniline nanofibers. *Mater. Lett.* **2008**, 62 (28), 4311–4314.
21. K. Gupta, P.C. Jana, A.K. Meikap. Optical and electrical transport properties of polyaniline-silver nanocomposite. *Synth. Met.* **2010**, 160 (13–14), 1566–1573.

22. S. Ghosal, P. Bhattacharyya. ZnO/RGO Heterojunction Based near Room Temperature Alcohol SENSOR with Improved Efficiency. *Eng. Proc.* **2021**, 6 (1), 25.
23. J. van den Broek, S. Abegg, S.E. Pratsinis, A.T. Güntner. Highly selective detection of methanol over ethanol by a handheld gas sensor. *Nat. Commun.* **2019**, 10 (1), 4220.
24. F. Sarf. Metal Oxide Gas Sensors by Nanostructures. In *Gas Sensors*; **2020**.
25. K.J. Choi, H.W. Jang. One-dimensional oxide nanostructures as gas-sensing materials: Review and issues. *Sensors*. 2010, pp 4083–4099.
26. T. Sen, S. Mishra, N.G. Shimpi. Synthesis and sensing applications of polyaniline nanocomposites: A review. *RSC Advances*. 2016, pp 42196–42222.
27. J. Rovner. Agency for Toxic Substances and Disease Registry (ATSDR). In *Health Care Policy and Politics A to Z*; CQ Press, 2300 N Street, NW, Suite 800, Washington DC 20037 United States, **2013**.
28. C. Malins, A. Doyle, B.D. MacCraith, et al. Personal ammonia sensor for industrial environments. *J. Environ. Monit.* **1999**, 1 (5), 417–422.
29. Y. Alarie. Dose-response analysis in animal studies: prediction of human responses. *Environ. Health Perspect.* **1981**, 42, 9–13.
30. L. Kumar, I. Rawal, A. Kaur, S. Annapoorni. Flexible room temperature ammonia sensor based on polyaniline. *Sensors Actuators, B Chem.* **2017**, 240, 408–416.
31. B. Timmer, W. Olthuis, A. Van Den Berg. Ammonia sensors and their applications - A review. *Sensors Actuators, B Chem.* **2005**, 107 (2), 666–677.
32. Z. Duan, Y. Jiang, M. Yan, et al. Facile, Flexible, Cost-Saving, and Environment-Friendly Paper-Based Humidity Sensor for Multifunctional Applications. *ACS Appl. Mater. Interfaces* **2019**, 11 (24), 21840–21849.
33. E. Bracken. Combating humidity - The hidden enemy in manufacturing. *Sens. Rev.* **1997**, 17 (4), 291–298.
34. F.W. Zeng, X.X. Liu, D. Diamond, K.T. Lau. Humidity sensors based on polyaniline nanofibres. *Sensors Actuators, B Chem.* **2010**, 143 (2), 530–534.
35. R.E. Kirk, D.F. Othmer. Kirk-Othmer Encyclopedia of Chemical Technology (4th Edition). *Kirk-Othmer Encyclopedia of Chemical Technology*. 1958, pp 1–10.
36. J.F. Pankow, J.A. Cherry. DENSE CHLORINATED SOLVENTS and other DNAPLs in Groundwater: History, Behavior, and Remediation; **1996**.
37. K. Wetchakun, T. Samerjai, N. Tamaekong, et al. Semiconducting metal oxides as sensors for environmentally hazardous gases. *Sensors Actuators, B Chem.* **2011**, 160 (1), 580–591.
38. P.M. Rørvik, T. Grande, M.A. Einarsrud. One-dimensional nanostructures of ferroelectric perovskites. *Advanced Materials*. 2011, pp 4007–4034.
39. J.W. Fergus. Perovskite oxides for semiconductor-based gas sensors. *Sensors and Actuators, B: Chemical*. 2007, pp 1169–1179.
40. S.B. Karki, R.K. Hona, F. Ramezanipour. Effect of Structure on Sensor Properties of Oxygen-Deficient Perovskites, A2BB′O5 (A = Ca, Sr; B = Fe; B′ = Fe, Mn) for Oxygen, Carbon Dioxide and Carbon Monoxide Sensing. *J. Electron. Mater.* **2020**, 49 (2), 1557–1567.
41. A.A. Athawale, S. Pethkar, S. Sharma, C. Nirkhe. Chloroform vapour sensor based on copper/polyaniline nanocomposite. *Sensors Actuators, B Chem.* **2002**, 85 (1–2), 131–136.
42. A.A. Athawale, M. V. Kulkarni. Polyaniline and its substituted derivatives as sensor for aliphatic alcohols. *Sensors Actuators, B Chem.* **2000**, 67 (1), 173–177.
43. M. V. Kulkarni, A.A. Athawale. Poly(2,3-dimethylaniline) as a competent material for humidity sensor. *J. Appl. Polym. Sci.* **2001**, 81 (6), 1382–1387.
44. A.A. Athawale, V. V. Chabukswar. Acrylic acid-doped polyaniline sensitive to ammonia vapors. *J. Appl. Polym. Sci.* **2001**, 79 (11), 1994–1998.
45. V. V. Chabukswar, S. Pethkar, A.A. Athawale. Acrylic acid doped polyaniline as an ammonia sensor. *Sensors Actuators, B Chem.* **2001**, 77 (3), 657–663.
46. A.A. Athawale, S. V. Bhagwat, P.P. Katre, A.J. Chandwadkar, P. Karandikar. Aniline as a stabilizer for metal nanoparticles. *Mater. Lett.* **2003**, 57 (24–25), 3889–3894.
47. A.A. Athawale, P.P. Katre. Ag Dispersed Conducting Polyaniline Nanocomposite as a Selective Sensor for Ammonia. *J. Metastable Nanocrystalline Mater.* **2005**, 23, 323–326.
48. A.A. Athawale, S. V. Bhagwat, P.P. Katre. Nanocomposite of Pd-polyaniline as a selective methanol sensor. *Sensors Actuators, B Chem.* **2006**, 114 (1), 263–267.
49. D. V. Dharmadhikari, S.K. Nikam, A.A. Athawale. Template free hydrothermal synthesis and gas sensing application of lanthanum cuprate (La2CuO4): Effect of precursors on phase formation and morphology. *J. Alloys Compd.* **2014**, 590, 486–493.
50. K. Vaid, J. Dhiman, S. Kumar, K.H. Kim, V. Kumar. A novel approach for effective alteration of morphological features of polyaniline through interfacial polymerization for versatile applications. *Nanomaterials* **2020**, 10 (12), 1–15.
51. G. Li, C. Martinez, J. Janata, et al. Effect of Morphology on the Response of Polyaniline-based Conductometric Gas Sensors: Nanofibers vs. Thin Films. *Electrochem. Solid-State Lett.* **2004**, 7 (10), H44.
52. T. Sen, N.G. Shimpi, S. Mishra, R. Sharma. Polyaniline/γ-Fe2O3 nanocomposite for room temperature LPG sensing. *Sensors Actuators, B Chem.* **2014**, 190, 120–126.
53. P. Kannusamy, S. Thambidurai. Chitosan-ZnO/polyaniline hybrid composites: Polymerization of aniline with chitosan-ZnO for better thermal and electrical property. *Polym. Degrad. Stab.* **2013**, 98 (5), 988–996.
54. W. Cho, S.J. Park, S. Kim. Effect of monomer concentration on interfacial synthesis of platinum loaded polyaniline nanocomplex using poly(styrene sulfonic acid). *Synth. Met.* **2011**, 161 (21–22), 2446–2450.
55. M.D. Bedre, S. Basavaraja, B.D. Salwe, et al. Preparation and characterization of Pani and Pani-Ag nanocomposites via interfacial polymerization. *Polym. Compos.* **2009**, 30 (11), 1668–1677.
56. J.M. Kinyanjui, N.R. Wijeratne, J. Hanks, D.W. Hatchett. Chemical and electrochemical synthesis of polyaniline/platinum composites. *Electrochim. Acta* **2006**, 51 (14), 2825–2835.
57. S. Mishra, N.G. Shimpi, T. Sen. The effect of PEG encapsulated silver nanoparticles on the thermal and electrical property of sonochemically synthesized polyaniline/silver nanocomposite. *J. Polym. Res.* **2013**, 20 (1), 49.
58. A.G. MacDiarmid, A.J. Epstein. The concept of secondary doping as applied to polyaniline. *Synth. Met.* **1994**, 65 (2–3), 103–116.
59. V. Svetlicic, A.J. Schmidt, L.L. Miller. Conductometric Sensors Based on the Hypersensitive Response of Plasticized Polyaniline Films to Organic Vapors. *Chem. Mater.* **1998**, 10 (11), 3305–3307.
60. S.A. Krutovertsev, S.I. Sorokin, A. V. Zorin, Y.A. Letuchy, O.Y. Antonova. Polymer film-based sensors for ammonia detection. *Sensors Actuators B. Chem.* **1992**, 7 (1–3), 492–494.
61. S.K. Dhawan, D. Kumar, M.K. Ram, S. Chandra, D.C. Trivedi. Application of conducting polyaniline as sensor material for ammonia. *Sensors Actuators, B Chem.* **1997**, 40 (2–3), 99–103.
62. J.G. Handique, L. Borah, R.J. Sarma, J.B. Baruah. Participation of self-generated polyaniline support in copper(II) catalysed oxidative reaction of phenyl aldimines. *J. Mol. Catal. A Chem.* **2002**, 188 (1–2), 63–69.
63. S.S. Barkade, J.B. Naik, S.H. Sonawane. Ultrasound assisted miniemulsion synthesis of polyaniline/Ag nanocomposite and its application for ethanol vapor sensing. *Colloids Surfaces A Physicochem. Eng. Asp.* **2011**, 378 (1–3), 94–98.
64. A. Choudhury. Polyaniline/silver nanocomposites: Dielectric properties and ethanol vapour sensitivity. *Sensors Actuators, B Chem.* **2009**, 138 (1), 318–325.
65. E. Mazario, P. Herrasti. Corrosion inhibition of aluminium by deposition of polypyrrole and silane compound. *J. Adv. Eng. Sci.* **2014**, No. May.
66. H.T. Hien, H.T. Giang, N. Van Hieu, T. Trung, C. Van Tuan. Elaboration of Pd-nanoparticle decorated polyaniline films for room temperature NH3 gas sensors. *Sensors Actuators, B Chem.* **2017**, 249, 348–356.

67. S. Jiang, J. Chen, J. Tang, et al. Au nanoparticles-functionalized two-dimensional patterned conducting PANI nanobowl monolayer for gas sensor. *Sensors Actuators, B Chem.* **2009**, 140 (2), 520–524.
68. M.D. Shirsat, M.A. Bangar, M.A. Deshusses, N. V. Myung, A. Mulchandani. Polyaniline nanowires-gold nanoparticles hybrid network based chemiresistive hydrogen sulfide sensor. *Appl. Phys. Lett.* **2009**, 94 (8), 083502.
69. A. Vijayan, M. Fuke, R. Hawaldar, et al. Optical fibre based humidity sensor using Co-polyaniline clad. *Sensors Actuators, B Chem.* **2008**, 129 (1), 106–112.
70. P. Ganguly, C.N.R. Rao. Electron transport properties of transition metal oxide systems with the K2NiF4 structure. *Mater. Res. Bull.* **1973**, 8 (4), 405–412.
71. S.K. Gupta, A. Joshi, M. Kaur. Development of gas sensors using ZnO nanostructures. *J. Chem. Sci.* **2010**, 122 (1), 57–62.
72. X. Hu, M. Li, Y. Xie, et al. Oxygen-Deficient Ruddlesden–Popper-Type Lanthanum Strontium Cuprate Doped with Bismuth as a Cathode for Solid Oxide Fuel Cells. *ACS Appl. Mater. Interfaces* **2019**, 11 (24), 21593–21602.

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