Review Article

Highly sensitive and selective chemiresistor gas/vapor sensors based on polyaniline nanocomposite: A comprehensive review

Sadanand Pandey a, b, *

a Department of Applied Chemistry, University of Johannesburg, P.O. Box 17011, Doornfontien 2028, Johannesburg, South Africa
b Centre for Nanomaterials Science Research, University of Johannesburg, South Africa

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ABSTRACT

This review article directs particular attention to some current breakthrough developments in the area of gas sensors based on polyaniline (PANI) nanocomposite. Conducting polymers symbolize a paramount class of organic materials that boost the resistivity towards external stimuli. Nevertheless, PANI-based sensor experiences some disadvantages of relatively low reproducibility, selectivity, and stability. In order to overcome these restrictions, PANI was functionalised or incorporated with nanoparticles (NPs) (metallic or bimetallic NPs, metal oxide NPs), carbon compounds (like CNT or graphene, chalcogenides, polymers), showing improved gas sensing characteristics. It has been suggested that host–guest chemistry combined with the utilization of organic and inorganic analog in nanocomposite may allow for improvement of the sensor performance due to synergetic/complementary effects. Herein, we summarize recent advantages in PANI nanocomposite preparation, sensor construction, and sensing properties of various PANI nanocomposite-based gas/vapor sensors, such as NH3, H2, HCl, NO2, H2S, CO, CO2, SO2, LPG, vapor of volatile organic compounds (VOCs) as well as chemical warfare agents (CWAs). The sensing mechanisms are discussed. Existing problems that may hinder practical applications of the sensors are also discussed.

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1. Introduction

Quickly expanding ecological pollution has been perceived as a paramount concern, and its monitoring has turned into a prime concern for human wellbeing. Advancement of gas detecting gadget is the earnest requirement for miniaturized, reliable, low-cost, compact electronic sensor procedures for a wide scope of uses, for example, air quality monitoring, medical diagnostics, control of food quality or safety of industrial processes and homemade security system [1–8].

Gas sensors are essentially made up of two types, which are based on (i) organic conducting polymers and (ii) inorganic metal oxides. Gas sensors using organic conducting polymers [for example, polyaniline (PANI), poly (3,4-ethylene-dioxythiophene) (PEDOT), polypyrrole (PPy), polythiophenes (PTs), etc.] of coveted functionality and conductivity keep on improving gas detecting performance [9–11]. Although they are sometime found to be unstable and show relatively poor sensitivity [12] due to the huge affinity of conducting polymers towards volatile organic compounds (VOCs) and moisture present in the environment. Gas sensors using inorganic metal oxides, such as tungsten oxide, zinc oxide, tin oxide, titanium oxide, iron oxide, silicon oxide, etc., show enhanced detecting qualities because of changing oxygen stoichiometry and electrically active surface charge [13,14]. However, these sensors work at high temperatures (~300–400 °C), regularly prompting to baseline drift and oxidation of analytes [15]. The operation of these devices at elevated temperatures causes gradual changes in the properties of the metal oxide nanostructures. The high-temperature operation can cause fusion of grain boundaries, which can avert the stability of the nanostructure and shorten the lifetime of the sensing device. In addition, the operation of such devices at elevated temperatures requires a distinct temperature controlled complex heating assembly and consumes extra power for heating purposes. Though possessing high sensitivity, the
utilization of such sensors for certain applications is exceptionally restricted.

The shortcomings of organic materials, such as low conductivity and poor stability, and of inorganic materials, such as the need for operation at high-temperature and sophisticated processability forestall them in gas sensor fabrication. In this context, the use of a nanocomposite composed of these two types of materials may promote effective gas sensing peculiarity and allow the sensor to be operational at low temperature. In the present article, we are specifically focusing on nanocomposites based on conducting polymer (PANI). PANI, which is a well-known conducting polymer, plays a major role in gas sensing applications due to the ease of synthesis and its potential to detect various gases [16]. PANI can exist in two different emeraldine classes of compounds, where the insulating emerald base form ($\sigma < 10^{-5}$ S/cm) can be converted into metallic, emeraldine salt conducting form ($\sigma < 1000$ S/cm) by protonic acid doping process (Fig. 1) [17–21].

PANI structures, such as nanowires (NWs) and nanoparticles (NPs) were suggested to strengthen the response time of the sensor by increasing the surface-to-volume ratio. But PANI-based sensor experiences some disadvantages (relatively low reproducibility, selectivity, and stability). In order to overcome these restrictions, PANI was functionalised or incorporated with NPs (metallic or bimetallic NPs, metal oxide NPs), carbon compounds (CNT or graphene, chalcogenides, polymers). From the literature, it is clear that PANI nanocomposites containing inorganic NPs result in the enhancement of gas sensitivity [22–24]. It has also been reported that the properties of PANI can be modified by NPs in two different ways. In the first place, n-type semiconducting NPs (e.g. WO₃, TiO₂, SnO₂) may bring about the development of p–n heterojunctions at PANI/NPs interfaces [25]. Thus, depletion regions may appear at PANI/TiO₂ interfaces. Because of the low local density of charge carriers, conductivity in depletion regions is generally poor. At the point, when PANI is influenced by deprotonating gas (e.g. NH₃) a width of depletion regions increases, which increases the sensor response. The second impact of NPs transfers on their catalytic properties. Interaction amongst PANI and specific gas is encouraged by gas particles adsorbed on a NP surface. Distinctive nanocomposite structures were proposed to include catalytic inorganic NPs [25–28].

In a previous couple of years, different types of sensor have been being developed using conducting polymers in different transduction modes. They are the potentiometric mode, the amperometric mode, the colorimetric mode, the gravimetric mode and the conductometric mode. In this review, we will consider exclusively the conductometric mode, where the gas detection is through the change of the electrical conductivity of the conducting polymer. The change of the electrical conductivity can result from charge-transfer with gas molecules or the mass change due to the physical adsorption of the gas molecules.

This review focuses on PANI-based nanocomposite gas/vapor sensors for environmental monitoring. Fig. 2 illustrates the PANI-based nanocomposite used to detect a wide range of gases and vapors.

2. PANI-based nanocomposite gas/vapor sensors

PANI-based nanocomposite has shown excellent sensing response to NH₃, H₂, HCl, NO₂, H₂S, CO, CO₂, SO₂, LPG, and volatile organic compounds (VOCs). Subsequently, some information from related works such as detection limit, sensing range, response time ($t_{\text{res}}$)/recovery time ($t_{\text{rec}}$), repeatability, and stability are likewise concisely and carefully posed and discussed. Efforts have been made to exploit these sensitivities in the development of new sensor technologies. Table 1 summarizes recent studies on diverse PANI nanocomposites with possible applications as gas/vapor sensors.

2.1. PANI-based nanocomposite for ammonia (NH₃) detection

Ammonia (NH₃) is a colorless gas and water-soluble with a characteristic pungent smell. Inhalation of NH₃ gas for longer time may cause various health-related issues, such as acute respiratory conditions (laryngitis, tracheobronchitis, bronchiolitis, bronchopneumonia and pulmonary edema), strong irritating effect over our eyes, noses, mouths, lungs and throats, which can further give rise to headache, vomiting, dyspnea, pneumonia-edema and even death [29,30]. The Occupational Safety and Health Administration (OSHA) have stipulated that the specified threshold limit value for NH₃ in the workplace is 50 ppm. NH₃ is known to be one of the important industrial raw materials used

Fig. 1. The two different emeraldine classes of PANI (A) non-conducting emeraldine base form and (B) conducting emeraldine salt form.
in the production of basic chemicals, textiles, fertilizer, paper products and sewage treatment [31]. In the case of explosives, ammonium nitrate gradually decomposes and releases trace amounts of NH3, which if detected would be helpful in explosion detection. Thus due to the harmful effect of NH3 related to human health, the environment and use in explosives, stringent action need to be urgently taken in order to monitor the trace level of NH3.

Recently, a great deal of efforts has presented a great leap forward in the development of PANI nanocomposite based gas sensors for NH3 detection. Kumar et al. [32] reported an NH3 gas sensor, which was fabricated by using chemically synthesized gold nanostars (AuNS) as catalysts and showed that they enhance the sensing activity of insulating PANI thin films. It was observed that the use of AuNS increased the sensitivity for the same concentration level of NH3, compared to that using gold nanorods (AuNR) and spherical AuNPs. For 100 ppm NH3, the sensitivity of the AuNS-PANI (AuNS ~ 170 nm) composites increased up to 52%. The AuNS-PANI composite even showed a rise as short as 15 s at room temperature (RT).

Jiang et al. [22] reported the manufacturing of 2D-ordered, large effective surface area, free-standing and patterned nanocomposite platform of PANI nanobowl-AuNPs (15 nm) which was self-assembled onto polystyrene spheres at the aqueous/air interface as a template and utilized for NH3 detection (0–1600 ppm). The sensor with a thickness of ~100 nm displayed a quick response time (t_res) of 5 s with a recovery time (t_rec) of 7 s at 100 ppm of NH3. Response results were found to be enhanced.

Tai and his team investigated NH3 gas-sensing behaviors of PANI/TiO2 nanocomposite synthesized by an in-situ chemical oxidation polymerization approach, of which the sensitivity (S) and the recovery time (t_rec) were enhanced by the deposition of TiO2 NPs on the surface of PANI films [33]. The thin film of PANI/TiO2 nanocomposite reports the improved conductivity contrasted with the pristine PANI film, inferring that an expansion of the conjugation length in PANI chains and the effective charge transfer amongst PANI and TiO2 may bring about an increment of conductivity. The authors presented the response and recovery property of the PANI/TiO2 sensor for the various concentrations of NH3 (23–141 ppm). It can be observed that the resistance of the sensor

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**Fig. 2.** Illustration of the PANI-based nanocomposite used to detect gasses for sensing applications.
Table 1
Sensor response (S), response time (t_{res}), recovery time (t_{rec}), studied detection range (DR), PANI based nanocomposite material (M) and operating temperature (T) of the various gas sensors.

<table>
<thead>
<tr>
<th>M</th>
<th>S (%)</th>
<th>t_{res} (s)</th>
<th>t_{rec} (s)</th>
<th>DR</th>
<th>T (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia (NH₃) detection</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI nanobowl–AuNPs (15 nm)</td>
<td>3.2 (100 ppm)</td>
<td>5</td>
<td>7</td>
<td>0–1600 ppm</td>
<td>RT</td>
<td>[22]</td>
</tr>
<tr>
<td>PANI/TiO₂</td>
<td>1.67 (23 ppm), 5.55 (117 ppm)</td>
<td>18</td>
<td>58</td>
<td>23–141 ppm</td>
<td>25 °C</td>
<td>[33]</td>
</tr>
<tr>
<td>Au/CNT–PANI</td>
<td>0.638 (25 ppm)</td>
<td>600</td>
<td>900</td>
<td>200 ppb–10 ppm</td>
<td>RT</td>
<td>[34]</td>
</tr>
<tr>
<td>NanoPANI-IDA</td>
<td>0.24 (100 ppm)</td>
<td>90</td>
<td>90</td>
<td>1–100 ppm</td>
<td>RT</td>
<td>[35]</td>
</tr>
<tr>
<td>SnO₂/PANI</td>
<td>16 (500 ppm)</td>
<td>12–15</td>
<td>80</td>
<td>100–500 ppm</td>
<td>RT</td>
<td>[36]</td>
</tr>
<tr>
<td>PANI/CSA–SNWs</td>
<td>50 (400 ppm at 0% RH)</td>
<td>–</td>
<td>–</td>
<td>10 ppb–400 ppm</td>
<td>24 °C</td>
<td>[37]</td>
</tr>
<tr>
<td>PANI/TiO₂/PANI/SnO₂ and PANI/In₂O₃</td>
<td>PANI/TiO₂ (1.5 for 23 ppm and 9 for 141 ppm); PANI/SnO₂ (1.2 for 23 ppm and 7 for 141 ppm); PANI/In₂O₃ (0.45 for 23 ppm and 1.35 for 141 ppm)</td>
<td>&gt;10 &gt;60</td>
<td>23–141 ppm</td>
<td>RT</td>
<td>[38]</td>
<td></td>
</tr>
<tr>
<td>PANI–SNWs</td>
<td>5.8 (50 ppb)</td>
<td>450</td>
<td>–</td>
<td>25–200 ppb</td>
<td>RT</td>
<td>[39]</td>
</tr>
<tr>
<td>TiO₂ microfibers encharged with PANI nanograins</td>
<td>0.004 (50 ppt)</td>
<td>–100</td>
<td>–</td>
<td>50–200 ppt</td>
<td>RT</td>
<td>[40]</td>
</tr>
<tr>
<td>TiO₂ nanograins</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI/TiO₂</td>
<td>12 (20 ppm)</td>
<td>72</td>
<td>–</td>
<td>340 s</td>
<td>RT</td>
<td>[41]</td>
</tr>
<tr>
<td>Core–shell PANI</td>
<td>0.11 (1 ppm)</td>
<td>150</td>
<td>300</td>
<td>20 ppb–10 ppm</td>
<td>25 °C</td>
<td>[42]</td>
</tr>
<tr>
<td>PANI–ZnO (50%)</td>
<td>–4.6 (20 ppm)</td>
<td>153</td>
<td>135</td>
<td>20–100 ppm</td>
<td>–</td>
<td>[43]</td>
</tr>
<tr>
<td>Graphene/PANI</td>
<td>3.65 (20 ppm), 11.33 (100 ppm)</td>
<td>50</td>
<td>23</td>
<td>1–6400 ppm</td>
<td>25 °C</td>
<td>[46]</td>
</tr>
<tr>
<td>MWNT/PANI</td>
<td>15.5</td>
<td>6</td>
<td>35</td>
<td>2 ppm</td>
<td>25 °C</td>
<td>[48]</td>
</tr>
<tr>
<td>(cellulose/TiO₂/PANI) Composite</td>
<td>6.3 (250 ppm)</td>
<td>36</td>
<td>18</td>
<td>100 ppb–100 ppm</td>
<td>12–40 °C</td>
<td>[50]</td>
</tr>
<tr>
<td>(PPA@CC–PPA)/PANI Nanocomposite</td>
<td>–5 (10 ppm)</td>
<td>10</td>
<td>46</td>
<td>5–2500</td>
<td>25 °C</td>
<td>[51]</td>
</tr>
<tr>
<td>PANI/NiTiPc</td>
<td>0.60 (5 ppm), 2.75 (100 ppm)</td>
<td>10</td>
<td>46</td>
<td>5–2500</td>
<td>25 °C</td>
<td>[51]</td>
</tr>
<tr>
<td>CSA doped PANI–SnO₂</td>
<td>0.91 (100 ppm)</td>
<td>46</td>
<td>3245</td>
<td>10–100</td>
<td>30 °C</td>
<td>[54]</td>
</tr>
<tr>
<td>Si/PANI</td>
<td>0.8 (20 ppm) 1.7 (90 ppm)</td>
<td>25</td>
<td>360</td>
<td>10–90</td>
<td>25 °C</td>
<td>[55]</td>
</tr>
<tr>
<td>p–MWNT/PANI</td>
<td>0.015 (20 ppm), 0.075 (100 ppm)</td>
<td>100</td>
<td>700</td>
<td>0–100</td>
<td>25 °C</td>
<td>[56]</td>
</tr>
<tr>
<td>S, N: GO/Ep/PANI hybrid</td>
<td>42.3 (100 ppm), 385 (1000 ppm)</td>
<td>115</td>
<td>44</td>
<td>1–1000</td>
<td>25 °C</td>
<td>[58]</td>
</tr>
<tr>
<td>Hydrogen (H₂) detection</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphene/PANI nanocomposite</td>
<td>16.57 (15% H₂)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>24 °C</td>
<td>[63]</td>
</tr>
<tr>
<td>Polyaniline (emeraldine)/anatase</td>
<td>1.63 (0.8% H₂)</td>
<td>83</td>
<td>130</td>
<td>–</td>
<td>RT</td>
<td>[64]</td>
</tr>
<tr>
<td>TiO₂ nanocomposite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al–SnO₂/PANI composite nanofibers</td>
<td>–275 (1000 ppm)</td>
<td>2</td>
<td>2</td>
<td>–</td>
<td>48 °C</td>
<td>[65]</td>
</tr>
<tr>
<td>CNT doped PANI</td>
<td>1.07 (2%)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[66]</td>
</tr>
<tr>
<td>Ta/PANI</td>
<td>1.42</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[67]</td>
</tr>
<tr>
<td>PANI/TiO₂/SnO₂</td>
<td>1.25 (0.8% H₂)</td>
<td>75</td>
<td>117</td>
<td>–</td>
<td>27 °C</td>
<td>[70]</td>
</tr>
<tr>
<td>Chitosan/PANI composite</td>
<td>130 (4% H₂)</td>
<td>–</td>
<td>–</td>
<td>0.3%–4%</td>
<td>RT</td>
<td>[94]</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl) detection</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>HCHO/PANI composite</td>
<td>800 (20 ppm)</td>
<td>10</td>
<td>–</td>
<td>0.01–100 ppm</td>
<td>RT</td>
<td>[98]</td>
</tr>
<tr>
<td>Nitrogen oxides (NO₂) detection</td>
<td></td>
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<td></td>
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<tr>
<td>PANI/MWNT/TiO₂</td>
<td>23.5 (25 ppm)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>22 °C</td>
<td>[99]</td>
</tr>
<tr>
<td>SnO₂–ZnO (20 wt %)/PANI</td>
<td>368.9 (35 ppm)</td>
<td>9</td>
<td>27</td>
<td>–</td>
<td>180 °C</td>
<td>[100]</td>
</tr>
<tr>
<td>1% PANI–SnO₂ sensor</td>
<td>3.01 × 10⁻³ (10 ppm)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>40 °C</td>
<td>[103]</td>
</tr>
<tr>
<td>SnO₂/PANI</td>
<td>4 (37 ppm)</td>
<td>17</td>
<td>25</td>
<td>5–55 ppm</td>
<td>140 °C</td>
<td>[104]</td>
</tr>
<tr>
<td>Hydrogen disulphide (H₂S) detection</td>
<td></td>
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<tr>
<td>CSA–doped PANI–CdS</td>
<td>76 (100 ppm)</td>
<td>–</td>
<td>413</td>
<td>10–100 ppm</td>
<td>RT</td>
<td>[107]</td>
</tr>
<tr>
<td>Flexible PANI–Ag</td>
<td>100 (10 ppm)</td>
<td>360 s</td>
<td>1–25 ppm</td>
<td>RT</td>
<td>[109]</td>
<td></td>
</tr>
<tr>
<td>Volatile organic compounds (VOCs) detection</td>
<td></td>
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<tr>
<td>Chloroform (CHCl₃) detection</td>
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<tr>
<td>PAN/Cu nanocomposite</td>
<td>1.5 (10 ppm)</td>
<td>–</td>
<td>–</td>
<td>10–100 ppm</td>
<td>–</td>
<td>[25]</td>
</tr>
<tr>
<td>Methanol (CH₃OH) detection</td>
<td></td>
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<td></td>
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<tr>
<td>PANI/Pd nanocomposite</td>
<td>104 (2000 ppm)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[27]</td>
</tr>
<tr>
<td>Trimethylamine (CH₃₂N) detection</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PANI/TiO₂</td>
<td>5.14 × 10⁻⁷ ML⁻¹</td>
<td>180</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[115]</td>
</tr>
<tr>
<td>Formaldehyde (HCHO) detection</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PANI)xMo₃O₉, on LLA04 (100) (LAO) substrate. (PANI)xMo3O9, thin films</td>
<td>8 (50 ppm)</td>
<td>600</td>
<td>–</td>
<td>–</td>
<td>30 °C</td>
<td>[116]</td>
</tr>
<tr>
<td>(PANI)xMo₃O₉, thin films</td>
<td>6 (25–400 ppb)</td>
<td>–</td>
<td>–</td>
<td>25–400 ppb</td>
<td>30 °C</td>
<td>[119]</td>
</tr>
<tr>
<td>Aromatic hydrocarbon detection</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI-MWNT (mass ratio 4:1)</td>
<td>0.31 (1000 ppm)</td>
<td>–</td>
<td>–</td>
<td>200–1000 ppm</td>
<td>RT</td>
<td>[122]</td>
</tr>
<tr>
<td>Liquid petroleum gas (LPG) detection</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PANI/TiO₂</td>
<td>63 (0.1 vol%)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[125]</td>
</tr>
<tr>
<td>PANI/CdSe</td>
<td>80 (1040 ppm)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[126]</td>
</tr>
<tr>
<td>PANI/ZnO</td>
<td>81 (1040 ppm)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[127]</td>
</tr>
<tr>
<td>p–PANI/n–TiO₂</td>
<td>63 (0.1 vol%)</td>
<td>140</td>
<td>–</td>
<td>(0.02–0.1 vol%)</td>
<td>RT</td>
<td>[126]</td>
</tr>
<tr>
<td>PAN/g–Fe₂O₃</td>
<td>1.3 (200 ppm)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[128]</td>
</tr>
<tr>
<td>PANI/ZnMo₃O₄</td>
<td>20.6–45.8 (800–1800 ppm)</td>
<td>600</td>
<td>840</td>
<td>(800–1800 ppm)</td>
<td>RT</td>
<td>[129]</td>
</tr>
<tr>
<td>PANI/ZnO</td>
<td>7.33 (1000 ppm)</td>
<td>100</td>
<td>185</td>
<td>–</td>
<td>RT</td>
<td>[130]</td>
</tr>
<tr>
<td>n–CdTe/g–PANI</td>
<td>67.7 (0.14 vol%)</td>
<td>80–300</td>
<td>600</td>
<td>(0.02–0.14 vol%)</td>
<td>RT</td>
<td>[137]</td>
</tr>
<tr>
<td>PANI/Fe₂O₃</td>
<td>0.5 (50 ppm)</td>
<td>60</td>
<td>–</td>
<td>(50–200 ppm)</td>
<td>RT</td>
<td>[128]</td>
</tr>
<tr>
<td>PANI/Cu/ZnSnS₄</td>
<td>44 (0.06 vol%)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>RT</td>
<td>[138]</td>
</tr>
</tbody>
</table>
expanded drastically when exposed to NH\textsubscript{3} analyte, and afterward slowly diminished when NH\textsubscript{3} analyte was replaced via air. It was found that the response of the sensor at 60 °C diminished and deliberated at RT, which might be ascribed to the exothermic adsorption of NH\textsubscript{3} [33]. In most of the cases, sensor response (S) is generally defined as the ratio of the change in resistance (R\textsubscript{g}/R\textsubscript{a}) upon exposure to target analyte to the resistance (R\textsubscript{a}) of the sensor in clean carrier (dry N\textsubscript{2}) gas.

\[ S = \left( \frac{R_g}{R_a} \right) \times 100\% \] \hspace{1cm} (1)

where \( R_g \) and \( R_a \) are the resistances of the sensor in the presence of NH\textsubscript{3} and in a pure carrier gas (dry N\textsubscript{2}), respectively.

The typical experimental setup for the analyzing chemiresitive gas sensor is shown in Fig. 3. The film of the sensor is placed in a closed glass chamber and the electrical resistance of the sensor film is measured by a multimeter (Keithley meter) through two conductive needles when analyte gas is injected into the chamber.

S for the PANI/TiO\textsubscript{2} composite based sensors for NH\textsubscript{3} concentration (23 and 117 ppm) was found to be (1.67\%) and (5.55\%) respectively. Response time (t\textsubscript{res}) is the time required for the sensor to respond to a step concentration change from zero to a certain concentration value. Recovery time (t\textsubscript{rec}) is the time it takes for the sensor signal to return to its initial value after a step concentration change from a certain value to zero. The t\textsubscript{res} and t\textsubscript{rec} values of PANI/TiO\textsubscript{2} for an exposure of (117 ppm) NH\textsubscript{3} gas at RT (25 °C) were found to be 18 s and 58 s, respectively. It was also observed with exposure of NH\textsubscript{3} (23 ppm) at RT, showing a great reproducibility of the sensor. The results also confirm that the response, reproducibility, and stability of the PANI–TiO\textsubscript{2} film to NH\textsubscript{3} are superior to CO gas with a much smaller effect of humidity on the resistance of the PANI/TiO\textsubscript{2} nanocomposite [33].

Chang et al. [34] investigated the fabrication of Gold/PANI/Multiwall carbon nanotube (Au/CNT-PANI) nanocomposite for online monitoring of NH\textsubscript{3} gas. The sensor exhibited a linear detection range from (200 ppb−10 ppm), a mean sensitivity of 0.638 (at 25 ppm), tres of 10 min, and trec of 15 min [34]. Thus the Au/CNT-PANI nanocomposite shows superior sensitivity and good repeatability when repeatedly exposed to NH\textsubscript{3} gas. The sensing mechanism for the Au/CNT-PANI nanocomposite is associated with the protonation/deprotonation phenomenon. As NH\textsubscript{3} gas is injected, NH\textsubscript{3} gas molecules withdraw protons from N\textsuperscript{+}H sites to form firmly more favorable NH\textsubscript{4}+... This deprotonation process reduces PANI from the emeraldine salt state to the emeraldine base state, leading to the reduced hole density in the PANI and thus an increased resistance. When the sensor is purged with dry
air, the process is reversed, NH$_4^+$ decomposes to form NH$_3$ and a proton, and the initial doping level and resistance recover.

Crowley et al. [35] used screen printing and inkjet printing methods to fabricate the NanoPANI-modified interdigitated electrode arrays (nanoPANI–IDAs) for NH$_3$ sensing at RT. The sensor was reported to show a stable logarithmic response to an analyte (NH$_3$) in the concentration of (1–100 ppm). The Sensor response for Inkjet-printed PANI thin films sensors for NH$_3$ (100 ppm) was found to be 0.24%. The $t_{res}$ and $t_{rec}$ characteristics of Inkjet-printed PANI thin films for (100 ppm) of NH$_3$ gas at RT (25 °C) were found to be 90 s and 90 s, respectively [35]. Deshpande et al. [36] reported the synthesis of SnO$_2$/PANI nanocomposites by incorporating SnO$_2$ particles as colloidal suspensions in PANI through the solution route method for detecting NH$_3$ gas at RT. Schematic diagram of the formation of SnO$_2$/PANI nanocomposite thin films is shown in (Fig. 4).

I–V characteristics at RT for pure SnO$_2$, pure PANI, and SnO$_2$/PANI nanocomposite films is shown in Fig. 5a–c respectively. It can be clearly observed that there was no appreciable change in resistance for pure SnO$_2$ (Fig. 5a), while in the case of pure PANI the resistance changed largely within a minute when exposed to NH$_3$ gas (Fig. 5b). The I–V characteristics of the SnO$_2$/PANI nanocomposite films demonstrate a fascinating phenomenon that the resistance decreased in exposure to NH$_3$ (~300 ppm) (Fig. 5c). Moreover, the I–V behaviors of SnO$_2$/PANI nanocomposites reveal a diode-like exponential conductivity, which is a characteristic for percolation in disordered systems, wherein the electrical conductance is found to be governed by the hopping mechanism [36]. The sensitivity (S %) of SnO$_2$/PANI nanocomposite films, when exposed to NH$_3$ (500 ppm), was determined to be 16. In the event of SnO$_2$/PANI nanocomposite films, a smooth increment of response was seen up to 300 ppm, and it then remained almost unchanged. The SnO$_2$/PANI nanocomposite films have $t_{res}$ of 12–15 s and $t_{rec}$ of ~80 s. It appears that the SnO$_2$/PANI nanocomposite films indicated quicker $t_{rec}$ (a variable of 2) as compared to the PANI films. It was clearly observed that with exposure to NH$_3$ gas (100–500 ppm in air) at RT, the resistance of the PANI film increased, while that of the SnO$_2$/PANI film decreased [36].

Zhang et al. [37] fabricated a camphor sulphonic acid (CSA)-doped PANI–SWCNT nanocomposite-based gas sensor (diameter 17–25 nm) using electropolymerization for the selective and sensitive detection of NH$_3$. The NH$_3$ sensing tests were performed in the range of 10 ppb–400 ppm. The sensor response was found to be 50 for 400 ppm of NH$_3$ at 0% relative humidity (RH). The PANI (CSA)–SWNTs showed greater sensitivity because of an affinity of NH$_3$ to PANI. The selectivity of the sensor was studied using 1 ppm of NO$_2$, 3000 ppm of H$_2$O, and 1 ppm of H$_2$S. It was observed that PANI (CSA)–SWNTs showed no responses to at least 1 ppm NO$_2$, 3000 ppm H$_2$, and 1 ppm H$_2$S, which confirm the high selectivity of PANI (CSA)–SWNTs toward NH$_3$ sensing [37]. Tai et al. [38] fabricated nanocomposites of PANI with TiO$_2$, SnO$_2$, and In$_2$O$_3$ using the in situ self-assembly technique for NH$_3$ sensing (23–141 ppm). The sensor responses of different PANI nanocomposites have been reported i.e PANI/TiO$_2$ (1.5 for 23 ppm and 9 for 141 ppm); PANI/SnO$_2$ (1.2 for 23 ppm and 7 for 141 ppm) and PANI/In$_2$O$_3$ (0.45 for 23 ppm and 1.35 for 141 ppm). It was found that all PANI-based nanocomposite systems had the shorter $t_{res}$ (2–3 s) and $t_{rec}$ (23–50 s) with better reproducibility (4 cycles) and long-term stability (30 days) [38]. It has been assumed that p-type PANI and n-type oxide semiconductor may form a p–n junction and a positively charged depletion layer on the surface of inorganic nanoparticles is created. This would cause a lowering of the activation energy and enthalpy of physisorption for NH$_3$ gas, leading to the higher gas sensing attributes than pure PANI thin film.

Lim et al. [39] researched the electrical and NH$_3$ gas detecting properties of PANI–SWNTs utilizing temperature-dependent resistance and FET transfer characteristics. The detecting response due to the deprotonation of PANI was observed to be positive for NH$_3$ (25–200 ppb) and negative to NO$_2$ and H$_2$S. This sensitivity of the PANI–SWNTs sensor was found to be 5.8% for NH$_3$, 1.9% for NO$_2$, and 3.6% for H$_2$S with lower detection limits of 50, 500, and 500 ppb, individually [39]. It was also observed that the sensor response was found to decrease with the increase in the concentration of NH$_3$ from 75 min at 50 ppb to 1 min at 100 ppm, while $t_{rec}$ ranged from several minutes to a few hours depending on the concentration. The poor selectivity of this fabricated sensor restricts its further applications.

Gong et al. [40] prepared a P-type conductive PANI nanograft onto an electrospray n-type semiconductive TiO$_2$ fiber surface for NH$_3$ detecting. It can be seen that with the increase of NH$_3$ concentration, the sensitivity greatly increases. The sensitivities of the film were reported to be 0.018, 0.009, and 0.004 for 200, 100, and 50 ppt of NH$_3$ analyte, respectively. The reproducibility and recovery of the sensor were tested using 10 ppb of NH$_3$ for 5 cycles [40]. Pawar et al. [41] reported on the fabrication of PANI/TiO$_2$ nanocomposite for selective detection of NH$_3$. This nanocomposite sensor is found to exhibit good gas response towards an NH$_3$ concentration up to 20 ppm. The NH$_3$ detection range is from 20 ppm to 100 ppm. The sensor response for PANI/TiO$_2$ nanocomposite sensor for NH$_3$ (20 ppm and 100 ppm) was found to be 12 and 48%. The $t_{res}$ and $t_{rec}$ for film sensors for an exposure of (20 ppm and 100 ppm) of NH$_3$ gas at RT (25 °C) were found to be 72 s, 340 s and 41 s, 520 s, respectively. It was suggested that the response resulted from the creation of a positively charged depletion layer at the heterojunction of PANI and TiO$_2$ [41]. Wojkiewicz et al. [42] reported the NH$_3$ sensing in the range of ppb from fabricated core-shell nanostructured PANI-based composites. The NH$_3$ detection range is from 20 ppb to 10 ppm. The sensor response of the core-shell PANI thin film sensors for NH$_3$ 1 ppm was found to be 0.11%. The $t_{res}$ and $t_{rec}$ of Inkjet-printed PANI sensors for an exposure of 1 ppm of ammonia gas at RT were found to be 2.5 min and 5 min, respectively [42].

![Fig. 4. Schematic diagram of the formation of SnO$_2$/PANI nanocomposite thin films.](https://example.com/figure4.png)
improved stability, reproducibility, and mechanical strength amongst the reported composites. These (50%) nanocomposite possessed the superb gas response as essential parameters for gas detecting formation, surface to volume proportion and activity of the gas detecting was observed that morphology assumed a critical part in sensitivity of the gas detecting. It was viewed that the nanostructured ZnO NPs and no agglomeration in the PANI framework. It was observed that the nanocomposite detecting film morphology and electrical resistivity were controlled by voltammetric parameters and ANI concentration. FTIR spectra of the nanocomposite constituted the presence of chemical bonding between the NPs and polymer concentration. As a result of the presence of TiO2 NPs, the sensitivity of the gas detecting film morphology revealed the uniform distribution of the ZnO NPs and no agglomeration in the PANI framework. It was viewed that the nanocomposite film reached a 500% change in resistance at the use of 100 ppm of NH3 [45].

Wu et al. [46] fabricated the graphene/PANI nanocomposites as conductometric sensors for the detection of NH3. It was observed that the graphene/PANI-based sensor increased the resistance with exposure to different NH3 concentrations (1–6400 ppm). The indication of the higher sensitivity of the sensor can easily be proven based on 1 ppm of NH3 detection. The sensor response values of the graphene/PANI and PANI sensors were found to exhibit linearity for NH3 concentrations (1–6400 ppm). The sensor response for absorption of NH3 concentration (20 and 100 ppm) was found to be 3.65 and 11.33% respectively. As compared to the PANI film, the graphene/PANI sensor exhibited much faster response and showed excellent reproducibility for NH3 gas [46].

Fig. 5. I–V curves (in the presence of NH3 gas) for (a) SnO2, (b) PANI and (c) SnO2/PANI nanocomposites. [Reprinted with permission from Ref. [36]. Copyright 2009 Elsevier].
Abdulla et al. [48] reported the trace detection of ammonia by using a PANI/MWCNTs sensor. The author used in-situ oxidative polymerization method for the synthesis of the PANI/MWCNTs sensor by utilizing ammonium persulfate (APS) as an oxidizing agent. The procedure for the fabrication of the sensing material was provided in Fig. 6. PANI/MWCNTs synthesis involved following the steps: First, acid treatment of MWCNTs was performed in order to get de-bundling of CNTs due to the formation of −OH and −COOH groups on its surface to form carboxylated MWCNTs. Then carboxylated MWCNTs were mixed with ANI monomer by in-situ oxidative polymerization method, resulting in the formation of the PANI/MWCNT nanocomposite. The application in gas sensing of C-MWCNT and PANI/MWCNT based sensors was analyzed by using the changes in the resistance of the sensor upon adsorption of NH3 gas molecules at RT [48].

The $t_{res}$ and $t_{rec}$ characteristics of C-MWCNTs based sensors for an exposure of 2–10 ppm of NH3 gas at RT were found to be 965–1865 s and 1440–2411 s, respectively. In the case of PANI/MWCNT nanocomposite $t_{res}$ and $t_{rec}$ were found to be 6–24 s and 35–62 s respectively. This clearly depicts that the PANI/MWCNT nanocomposite shows very fast response and recovery time for NH3. Sensor response for C-MWCNTs and PANI/MWCNT composite based sensors was analyzed by using the changes in the resistance of the sensor upon adsorption of NH3 gas molecules at RT [48]. Authors suggested that the enhancement of sensing performance of PANI/MWCNTs can be related to the combined effect of doping/dedoping of PANI and the electron transfer between the NH3 molecules and MWCNT. The PANI/MWCNTs sensors show good reproducibility and reversibility after 5 cycles of repeated exposure and desorption of NH3 gas for 2 ppm NH3 gas. The sensor was found to be highly selective towards NH3 (15.5% for 2 ppm of NH3) among the other oxidizing/reducing gasses i.e H2S (2%), Acetone (5%), Isoprene (5.3%), Ethanol (5.6%) and NO2 (4%).

![Fig. 6. Schematic of the synthesis of PANI functionalized MWCNTs.](image)
and methanol [49]. It was reported that PANI is a p-type semiconductor, and TiO2 is n-type, during polymerization of ANI, which was operated with the cellulose/TiO2 composite nanofibers as templates, there would be P–N heterojunction formed at the interface between PANI and TiO2 NPs. So the P–N heterojunction may play an important role in the improvement of gas sensing properties of the cellulose/TiO2/PANI composite sensors. Thus when exposed to ammonia, the resistance of cellulose/TiO2/PANI composite nanofibers would increase not only because of the de-doping process but also the change in the depletion layer thickness of P–N heterojunction.

Guo et al. [50] fabricated a hierarchically nanostructured graphene–PANI (PPANI/rGO–FPANI) nanocomposite for detection of NH3 gas concentrations (100 ppb–100 ppm), dependable reliable transparency (90.3% at 550 nm) for the PPANI/rGO–FPANI nanocomposite film (6 h sample), fast response $t_{res}/t_{rec}$ (36 s/18 s), and strong flexibility without an undeniable performance decrease after 1000 bending/extending cycles. It was watched that amazing detecting performance of sensor could most likely be attributed to the synergetic impacts and the moderately high surface area ($47.896 \text{ m}^2 \text{ g}^{-1}$) of the PPANI/rGO–FPANI nanocomposite film, the productive artificial neural system detecting channels, and the adequately uncovered dynamic surfaces [50]. Zhihu et al. [51] investigated the NH3 sensing at RT by using porous thin film composites of PANI/sulfonated nickel phthalocyanine (PANI/NiTSPc), which were deposited across the gaps of interdigitated Au electrodes (IAE) by an electrochemical polymerization method. The sensor response of the PANI/NiTSPc film to 100 ppm NH3 was found to be 2.75 with a short $t_{res}$ of 10 s. The PANI/NiTSPc film sensor has significant properties of fast recovery rate, good reproducibility and acceptable long-term stability in the range from (5–2500 ppm). The outstanding sensing performance of the PANI/NiTSPc composites may be attributed to the porous, ultra-thin film structure [52,53] and the “NH3-capture” effect of the flickering NiTSPc molecules.

Khuspe et al. [54] reported NH3 sensing by using (PANI)-SnO2 nanohybrid-based thin films doped with 10–50 wt % camphor sulfonic acids (CSA), which were deposited on the glass substrates using spin coating technique. FESEM of PANI, PANiSnO2 (50%) and PANI–SnO2–CSA (30%) nanohybrid films at 100K magnification. The film of PANI has a fibrous morphology with high porosity. PANI–SnO2 (50%) nanocomposite, which shows the uniform distribution of SnO2 nanoparticles in the PANI matrix. The doping of CSA has a strong effect on the PANI–SnO2 nanocomposite morphology. The nanocomposite showed a transformation in morphology from fussy fibrous into clusters with an increase in CSA content in the case of PANI–SnO2–CSA (30%) nanohybrid. It was observed that the PANI–SnO2 hybrid sensor showed the maximum response of 72%–100 ppm NH3 gas operating at RT. A significant sensitivity (91%) and fast response (46 s) toward 100 ppm NH3 operating at room temperature was observed for the 30 wt % CSA doped PANiSnO2 nanohybrid film. The sensitivity of PANi–SnO2–CSA (10%), PANi–SnO2CSA (20%), PANi–SnO2–CSA (30%), PANi–SnO2–CSA (40%), PANi–SnO2–CSA (50%) nanohybrids to 100 ppm of NH3 gas were 80%, 86%, 91%, 84% and 75%, respectively, operating at RT.

Tai et al. [55] reported a P–P isotype heterojunction sensor for NH3 detection at RT, which was developed by modifying microstructure silicon array (MSSA) with self-assembled PANI nano-thin film. It exhibited the high response, good reversibility, repeatability and selectivity when exposed to NH3. The sensor response (S), $t_{res}$ and $t_{rec}$ of the sensor were determined to be about 0.8%, 25 s and 360 s to 20 ppm NH3 at 25 °C, respectively. The sensor response was found to be 0.8–1.7% from the concentration range of 10–90 ppm of NH3. Yoo et al. [56] investigated the effects of O2 plasma treatment on NH3 gas sensing characteristics (e.g. linearity, sensitivity, and humidity dependence) of p-MWCNT/PANI composite films. The sensor response, $t_{res}$ and $t_{rec}$ were determined to be about 0.015%, 100 s and 700 s to 20 ppm NH3 at 25 °C, respectively. The sensor response was found to be 0.01–0.075% from the concentration range of 0–100 ppm of NH3. These results indicate that
oxygen-containing defects on the plasma-treated MWCNTs play a crucial role in determining the response of the pF-MWCNT/PANI composite film to NH$_3$.

Huang et al. [57] studied the NH$_3$ sensing by using chemically reduced graphene oxide (CRG). Aniline was used to reduce graphene oxide (GO) in order to obtain CRGs attached with different states of PANI, i.e. acid-doped PANI attached CRG, de-doped PANI attached CRG and free CRG. The results clearly suggested that free CRG exhibited an excellent response to NH$_3$ and showed high sensitivity to NH$_3$ with the concentrations at parts-per-million (ppm) level. The sensors based on free CRG exhibited a response of 37.1% when exposed to 50 ppm of NH$_3$ at 25 °C. The sensor also showed high reproducibility and great selectivity. The fabrication and characterization of room temperature flexible NH$_3$ sensor based on S and N co-doped graphene quantum dots ((S, N: GQDs)/PANI) hybrid loading on flexible polyethylene terephthalate (PETP) thin film by chemical oxidative polymerization method were reported by Gavgani et al. [58]. The S and N co-doped graphene quantum dots (S, N: GQDs) were synthesized by hydrothermal process of citric acid and thiourea. The synthesis of S, N: GQDs and

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Fig. 8. Schematic diagram for the synthesis of S, N: GQDs (a); Schematic diagram for the gas sensor fabrication process of sensing devices based on S, N: GQDs/PANI hybrids (b). [Reprinted with permission from Ref. [58]. Copyright 2016 Elsevier].
S, N: GQDs/PANI hybrid are schematically shown in Fig. 8a and b respectively. In this study, S, N: GQDs/PANI water solution was drop casted over the PET film (1 cm × 1 cm). The solution was evaporated using vacuum oven at 80 °C for 1 h, interdigitated Au electrodes with 400 µm interdigit spacing, 100 nm thickness and 100 µm wide were deposited on a flexible PET substrate by physical vapor deposition method. Finally, the flexible hybrid gas sensor was baked for 1 h in a furnace at 80 °C in a N2 atmosphere. The details of the fabrication process of S, N: GQDs/PANI hybrid gas sensor are provided in Fig. 8b. The sensing response clearly depicts that S, N: GQDs/PANI hybrids have 5 times more sensitivity as compared with PANI at NH3 (100 ppm). The conductivities of hybrid and PANI at an 10 nA applied current are 32.8 S cm⁻¹ and 95.8 S cm⁻¹, respectively. It corresponds to a significant increase of charge carrier concentration due to S, N: GQDs incorporation. Thus, S, N: GQDs play a dominant role in the charge transport through the PANI matrix. The t_res and t_rec of the flexible pure PANI and S, N: GQDs/PANI gas sensors to 10 ppm of NH3 are 183 s, 77 s, and 115 s, 44 s, respectively. The sensor response of flexible pure PANI and S, N: GQDs/PANI hybrid gas sensors are 10.1% and 42%, respectively at 100 ppm NH3. The detection limit of NH3 gas for flexible pure PANI, and S, N: GQDs/PANI hybrid gas sensors are 1 ppm and 500 ppb, respectively at 25 °C in 57% relative humidity (RH). The GQDs/PANI hybrid shows high selectivity. It was observed that the sensor response of 100 ppm of NH3, toluene, methanol, acetone, ethanol, chlorobenzene, and propanol is 42.3, 0.5, 0.45, 0.5, 0.48, 0.51, and 0.48%, respectively. This indicates that the flexible S, N: GQDs/PANI hybrid gas sensor possesses very high response to NH3 but is almost insensitive to other VOC gasses.

2.2. PANI-based nanocomposite for hydrogen (H2) detection

Hydrogen is odorless, colorless, and tasteless gas, which is extremely explosive in an extensive range of concentration (4–75%) [59,60]. Hydrogen is utilized broadly as a part of scientific research and industry as the fuel for the internal combustion engines, rocket propellant, glass and steel manufacturing, shielding gas in atomic hydrogen welding, and rotor coolant in electrical generators, [61]. The main dangers associated with H2 gas include high permeability through many materials and flammability. Therefore, development of rapid, accurate, and highly sensitive hydrogen sensors to detect a leakage for safe storage, delivery, and utilization of hydrogen is exceedingly attractive so as to accomplish safe and effective processing of hydrogen on enormous scale. Sadek et al. [62] reported the chemical polymerization technique for the fabrication of PANI/WO3 nanocomposite on the surface of a layered ZnO/64% YX LiNbO3 substrate for monitoring H2 gas. The experimental process involves exposure of sensor with H2 gas pulse sequence of (0.06%, 0.12%, 0.25%, 0.50%, 1%, and 0.12%) in synthetic air at RT. It was observed that sensor response was approx. 7 kHz for 1% of H2 in synthetic air. The 90% t_res of 40 s and t_rec of 100 s with good reproducibility were observed at RT. It was found that the PANI/WO3 nanocomposite sensor produces repeatable responses of the same magnitude with good baseline stability [62]. Authors have proposed two possible mechanisms for H2 sensing. The first mechanism involves the activation of the H2 molecule by WO3 due to the formation of tungsten–dioxygen complexes. While the second possible mechanism can be due to the closer packing of PANI backbones by WO3, dissociation of the H2 molecule is stimulated by interaction with a free spin on adjacent PANI chains.

Al-Mashat et al. [63] fabricated the H2 gas sensor by using graphene/PANI nanocomposite. In the chemical route was followed for graphene synthesis; followed by ultra-sonication with a blend of ANI monomer in presence of APS (initiator) in order to form PANI on its surface. The SEM micrograph result clearly depicts that the composite has a nano-fibrillar morphology. The authors have found that the graphene/PANI nanocomposite-based gadget sensitivity is 16.57% toward 1% of H2 gas, which is much higher than the sensitivities of sensors based on just graphene sheets and PANI nanofibers. Nasrian & Moghadam reported the synthesis of PANI (emeraldine)/anatase TiO2 nanocomposite by a chemical oxidative polymerization [64]. The thin films of PANI (emeraldine)/anatase TiO2 nanocomposite for H2 gas sensing were deposited on Cu-interdigitated electrodes by spin coating technique at RT. The action and t_res/t_rec time of the sensors for H2 gas were assessed by the change of TiO2 wt% at natural conditions. Resistance-detecting estimation displayed a high sensitivity around 1.63, a great long-term response, low response time and recovery time around 83 s and 130 s, individually, at 0.8 vol% H2 gas for PANI/emeraldine/anatase TiO2 nanocomposite including 25 wt. of anatase NPs [64]. Sharma et al. [65] fabricated Al–SnO2/PANI composite nanofibers via electrospinning technique for H2 sensing. It can be clearly observed by experimental results that 1% Al–SnO2/PANI nanofibers have a better response for sensing of hydrogen as compared to that of 1% Al–SnO2 alone. The results depict that 1% Al–SnO2/PANI hybrid have high sensitivity (~275%) to H2 gas (1000 ppm) at 48 °C with relatively faster t_res (0.6 s) and t_rec (2.3 s). Srivastava et al. [67] reported on the development of interdigitated electrode (IDE) based chemiresistor type gas sensor and the thin films of PANI and CNT-doped PANI for H2 gas sensing at RT. The gas sensing measurements were performed towards 2% of hydrogen concentration in air at 1.3 atm hydrogen pressure at RT. The response of PANI film was observed around 1.03, which increased up to 1.06 and 1.07 for MWNT/PANI and SWNT/PANI composite films respectively. In the case of SWNT/PANI and MWNT/PANI composite films, the conducting paths were formed due to quantum mechanical tunneling effects and electron hopping occurred through conducting channels of CNT. The presence of SWNT and MWNT in PANI could promote the possibility of more H2 adsorption because of their centrally hollow core structure and their large surface area that provided more interaction sites within the PANI composite available for H2 sensing.

Srivastava et al. [67] reported the effect of Swift heavy ion (SHI) irradiation on the gas sensing properties of a tantalum (Ta)/PANI composite thin film based chemiresistor type gas sensor for H2 gas sensing application at RT. It was observed that the unirradiated Ta/PANI composite sensor showed negligible response. It could be due to the Ta layer coated over the PANI surface, which did not react with H2 at RT and inhibited the hydrogen to diffuse into the PANI matrix. Therefore at RT the pristine Ta/PANI sensor did not show any response to H2. While upon irradiation, it was observed that the Ta/PANI composite sensor showed a higher response and the response increased slightly with increasing ion fluence. The response value was reported to be −1.1 (i.e. % Sensitivity ~9.2%) for Ta/PANI composite sensor irradiated at fluence 1 × 10³ ion/cm², which was increased up to 1.42 (i.e. % Sensitivity ~30%) for composite sensor irradiated at fluence 1 × 10¹¹ ion/cm² (Fig. 9). It may suggest that due to the SHI irradiation Ta melt and diffused into the PANI matrix, which provided comparatively rough and higher surface area for hydrogen adsorption and rapid diffusion, therefore more interaction sites were available for hydrogen sensing and hence the sensing response was increased. It has been reported that the rough and fiber-like structure of PANI shows a faster and higher response for hydrogen than conventional PANI films, because the three-dimensional porous structure of a PANI nanofibers allows for easy and rapid diffusion of hydrogen gas into the PANI matrix [68,69]. Srivastava et al. [66] investigated the gas sensing at 27 °C by using an PANI/TiO2–SnO2 nanocomposite deposited onto epoxy glass substrate with Cu-interdigitated electrode. The schematic diagram of our handmade gas sensor setup is shown in Fig. 10. The
The typical structure of H$_2$ sensor consists of a layer of PTS on a finger type Cu-interdigitated electrodes patterned area of an epoxy glass substrate and two electrodes. The sensor response ($S$), response ($t_{res}$) and recovery time ($t_{rec}$) calculation are made in the same way as shown earlier. H$_2$ gas sensing results demonstrated that a PTS sensor with 20 and 10 wt % of anatase-TiO$_2$ and SnO$_2$ NPs, respectively, has the best $t_{res}$ (75 s) with a $t_{rec}$ of 117 s and has a sensitivity of 1.25 (0.8 vol% H$_2$). The human development has been grouped by paramount material on which the modern innovation is based like Stone Age, Iron Age and now the Polymer Age [71]. This age is properly called the polymer age because of a broad utilization of polymers in all domains of life [72–93]. Li et al. [94] reported the high sensitivity and high selectivity, and response towards H$_2$ gas using chitosan (biopolymer) in Chitosan/PANI composite at RT. The Chitosan/PANI composite and pure PANI structures in response to 4% H$_2$ gas diluted in air at RT shows the following results: Firstly resistance increased with the Chitosan/PANI composite while it decreased with the pure PANI upon exposure; secondly response with the Chitosan/PANI composite film was higher (at ~130%) than with the PANI at ~28%; The sensor response to the H$_2$ gas concentration ranging from 0.3 to 4% was found to be quite linear.

2.3. PANI-based nanocomposite for hydrochloric acid (HCl) detection

Hydrochloric acid (HCl) occurs as a colorless, non-flammable aqueous solution or gas. HCl is mostly used in different industrial sectors; it is extremely dangerous for both living beings and the environment. It was observed that exposure to concentrated HCl may even be fatal because of circulatory collapse or asphyxia caused by glottic edema [95]. Low concentrations of HCl solutions exposure may cause different health problems such as conjunctivitis, corneal burns, ulceration of the respiratory tract, dermatitis, skin burns, bronchitis, pulmonary edema, dental erosion,

![Fig. 9. Response versus time plot for unirradiated and irradiated Ta/PANI composite sensors after hydrogen exposure at RT. [Reprinted with permission from Ref. [67]. Copyright 2012 Elsevier].](image-url)

![Fig. 10. The schematic block diagram of our handmade hydrogen gas sensing setup. [Reprinted with permission from Ref. [70]. Copyright 2015 Elsevier].](image-url)
hoarseness, nausea, vomiting, abdominal pain, diarrhea, permanent visual damage etc. [95,96]. The airborne permissible exposure limit (PEL) for HCl is 5 ppm in 8 hr work day. A concentration of 100 ppm is known to be immediately dangerous to life or health (IDLH) [97]. Thus there is a need for developing HCl sensors. Mishra et al. [98] fabricated a specific, quick and sensitive HCl gas sensor by utilizing nanocomposites of copolymers of ANI and HCHO prepared with a metal complex of Fe−Al (95:05) by means of thermal vacuum evaporation deposition techniques. This sensor detects HCl (0.2–20 ppm) in 8–10 s. These nanocrystalline composite film displayed high sensitivity (400−800) and a tres of 10 s. The selectivity was accomplished by appropriate doping of PANI during synthesis. The sensor was reusable, as there was no chemical reaction between PANI film and HCl gas. Moreover, the sensor worked at RT and had a broadened lifetime.

2.4. PANI-based nanocomposite for nitrogen oxide (NOx) detection

Nitrogen oxides include the gasses nitrogen oxide (NO) and nitrogen dioxide (NO2). NO2 forms from ground–level emissions results of the burning of fossil fuels from vehicles, power plants, industrial sources, and off-road equipment. NO2 cause harmful effects on human health and the environment. Exposure of NO2 causes several respiratory system problems in human beings. On January 22, 2010, EPA strengthened the health based National Ambient Air Quality Standard (NAAQS) for NO2. EPA set a 1-h NO2 standard at the level of 100 ppb. EPA also retained the annual average NO2 standard of 53 ppb. Yun et al. [99] investigated the sensing of NO by fabricating PANI/MWCNT/TiO2 composite using in situ polymerization method. The electrical resistance decreased upon NO gas exposure which is the typical characteristics of a p-type semiconductor. The decrease in the electrical resistance is attributed to the electron charge transfer between NO gas and the surface of PANI/MWCNT p-type semiconductors. PANI/MWCNT/TiO2 composite sensor shows the highest sensitivity of 23.5% to NO (25 ppm) at 22 °C. The sensor showed excellent reproducibility in gas sensing behavior during the recovery process at a lower temperature of 100 °C.

Xu et al. [100] demonstrated the NO2 sensing by using a SnO2−ZnO/PANI composite thick film. The SnO2−ZnO/PANI composite was fabricated from SnO2−ZnO porous nano solid and PANI by a conventional coating method. The SnO2−ZnO composite porous nanosolid was synthesized by a solvo-thermal hot-press technique. It was observed that the sensor based on SnO2−ZnO/PANI composite sensor showed high stability to NO2 (35 ppm) monitored for 22 min at 180 °C. The sensor response to 35 ppm NO2 increased from (40–180 °C) and started decreasing after further increasing temperature. SnO2−ZnO (20 wt %)/PANI composite sensor has the highest sensor response (%S) of 368.9 at 180 °C. Selectivity study of the sensor was also performed at 180 °C by using different analytes (NO2, NH3, H2, C2H5OH, and CO). It was observed that sensor response of analytes (NH3, H2, C2H5OH, and CO) was below 3%, while that of NO2 exhibited an extremely high sensor response of 368.9. The results depict that the SnO2−ZnO (20 wt %)/PANI composite based sensors have high sensitivity (368.9%) to NO2 (35 ppm) at 180 °C with relatively fast tres (9 s) and trec (27 s).

WO3−PANI and hemin/ZnO-PPy nanocomposite thin film sensors were prepared by Kaushik et al. [101] and Prakash et al. [102] respectively, to detect NOx gases. The NOx gas sensing characteristics of the sensors were performed by measuring the change in resistance w.r.t time. This sensor exhibited a linear range of 0.8−2000 μM, a sensitivity of 0.04 μM−1 and a detection limit of 0.8 μM at RT. Sharma et al. [103] showed the gas detecting properties of (0.5−3% PANI)-SnO2 sensors for trace NO2 gas detection. It was accounted for that (1% PANI)-SnO2 sensor film indicated high sensitivity towards NO2 gas alongside a sensitivity of 3.01 × 104 at 40 °C for 10 ppm of gas. On introduction of NO2 gas, the resistance of all sensors expanded to a substantial degree, considerably more prominent than three orders of magnitude. After removal of NO2 gas, changes in resistance were observed to be reversible in nature and the fabricated composite film sensors demonstrated great sensitivity with moderately quicker tres/trec [103].

The NO2 detection by using a SnO2/PANI double-layered film sensor fabricated using nanoporous SnO2 and PANI layers was reported by Xu et al. [104]. This double-layered film sensor showed high selectivity and high response to NO2 gas even with low concentration. The sensor response, tres and trec time of sensor S5P500 are as short as about 4%, 17 s and 25 s to 37 ppm NO2 at 140 °C, respectively. The sensor response was found to be 1−13% from the concentration range of 5−55 ppm of NO2. Selectivity of the sensor was studied using 1000 ppm CO, 1000 ppm H2, 1000 ppm, C2H5OH vapor, 10 ppm NO2 and 10 ppm NH3. It was observed that S5P100 had a comparatively strong response to 10 ppm NO2, but no response to other gases as the working temperature was lower than 180 °C. Reproducibility of two sensor S5P100 & S5P500 to 37 ppm of NO2 at 140 °C was performed. The sensors show high reproducibility up to four cycles (Fig. 11). The mechanism for NO2 sensing enhancement may be due to the formation of the depletion layer at the p–n junction interface in SnO2/PANI double layered film sensor, which makes a great resitivity difference in air and NO2 gas.

2.5. PANI-based nanocomposite for hydrogen disulfide (H2S) detection

Hydrogen sulfide (H2S) is a colorless, flammable, and extremely hazardous gas. It occurs naturally in crude petroleum, natural gas, and hot springs. Exposure to low concentrations of H2S causes irritation in the eyes, nose, throat and respiratory system (e.g., burning/tearing of eyes, cough, shortness of breath). High concentrations of H2S can cause shock, convulsions, inability to breathe, extremely rapid unconsciousness, coma and death. The OSHA has stipulated that the specified threshold limit value for H2S in the workplace is 20 ppm. A level of H2S gas at or above 100 ppm is IDLH. Thus monitoring of H2S is very important. Shirsat et al. [105] reported the PANI nanowires bridging the 3 μm gap between
two Au IDEs, which were synthesized using a two-step galvano-
static electrochemical polymerization technique. Nanowire net-
works were further functionalized by controlled growth of AuNPs of size ~70–120 nm. PANI/Au nanocomposite exhibited an outstanding response to H$_2$S gas (~0.1 ppb) with good selectivity and reproducibility [105]. Authors have proposed a plausible mechanism for the formation of AuS [Eq. (2)] and subsequent protonation of PANI for H$_2$S detection by PANI/Au nanocomposites.

$$\text{H}_2\text{S} + \text{Au} \rightarrow \text{AuS} + 2\text{H}^+ \quad (2)$$

The authors suggested that transfer of electrons from PANI to Au led to a drop in resistance of the material.

Crowley and coworkers developed PANI/CuCl$_2$ sensor printed on screen printed interdigitated electrodes for trace level H$_2$S detection. H$_2$S exerted an oxidizing effect on PANI due to preferential binding of CuCl$_2$ with S$^2-$ ion with the evolution of HCl, which protonated PANI increasing its electrical conductivity [106]. Raut and his co-workers reported a CSA-doped PANI–CdS nanocomposite synthesized by chemical polymerization for the selective detection of H$_2$S (10–100 ppm) [107]. This sensor exhibited a maximum response of 76% at 100 ppm and 97.34% stability after 10 days for 40% doping of CSA in the PANI–CdS nanocomposite. The CSA–PANI–CdS sensor exhibited negligible response (2–5%) to NO$_2$, CH$_3$OH, C$_2$H$_5$OH, and NH$_3$. Unfortunately, however, this sensor possesses a high recovery time of ~205–413 s.

Raut et al. [108] investigated H$_2$S sensor based on PANI–CdS nanocomposites fabricated by a simple spin coating technique at RT (300 K). The resistance of PANI–CdS nanocomposites showed a considerable change when exposed to various concentrations of H$_2$S. The sensor response of ~48% was achieved for 100 ppm H$_2$S for PANI–CdS sensor. Based on the concentration of H$_2$S, the $t_{rec}$ and $t_{res}$ were found to be in the range of (41–71 s) and (345–518 s) respectively. It can be clearly observed in the Fig. 12, that PANI–CdS nanocomposite films can sense the lower concentration of H$_2$S with higher sensitivity value as compared to the large concentration of other gasses. The plausible mechanism of selectivity for H$_2$S may be traced to the characteristics of vapor adsorbed over the surface of PANI–CdS nanocomposites.

Mekki et al. [109] fabricated flexible PANI–Ag nanocomposite films on (3-aminopropyl) trimethoxysilane (APTMS) modified biaxially oriented polyethylene terephthalate (BOPET) by in situ effortless UV prompted polymerization of ANI in the presence of AgNO$_3$. Low magnification SEM picture of PANI–Ag films (arranged with AgNO$_3$ 0.5 M) demonstrates the nano-brush morphology. I–V curves for these films are straight, demonstrating an ohmic contact between the Au electrode and PANI–Ag film. The chemiresistive gas detecting properties of PANI–Ag films were researched by the presentation of 10 ppm of every test gasses, for example, NH$_3$, H$_2$S, Cl$_2$, NO, NO$_2$, CO, CH$_4$, and C$_2$H$_5$OH. Among all gasses PANI–Ag films demonstrated the response to H$_2$S only. The expansion in current on presentation to H$_2$S (1–25 ppm) was observed [109]. The gas detecting results (for example, lowest detection limit (LDL) of 1 ppm with a high response 100% and quick response time 6 min at 10 ppm) were acquired. The mechanism for the interaction of H$_2$S with PANI-based composites can be clarified by dissociation of H$_2$S on the metal surface under surrounding condition since it is a weak acid (acid dissociation constant $pK_a$ = 7.05). The dissociation of H$_2$S results into H$^+$ and HS$^-$ ions. The subsequent HS$^-$ anion makes up for the positive N$^+$ charges in the PANI chains, however, there is additionally proton liberation in the films. Since the mobility of cation (H$^+$) is much bigger than the anion (HS$^-$), in this manner the general impact is the slight conductance ascend on presentation to H$_2$S.

2.6. PANI-based nanocomposite for volatile organic compounds (VOCs) detection

Volatile organic compounds (VOCs) are a standout amongst the most mainstream gasses whose detections are exceedingly attractive. There is, therefore, a surge of enthusiasm for the development of VOCs sensors in light of the fact that they continually risk our well-being as well as the environment around us and cause chronic health threats to human beings, animals and plants. Volatile organic compounds also contribute to climate change and destruction of the ozone layer [110,111]. The low flashpoints of VOCs make them particularly threatening in closed areas. Thus, there is an increasing demand for the development of a continuous real-time technique to monitor VOCs.

CHCl$_3$ vapors depress the central nervous system (CNS) of human beings and animals. Chronic chlorof orm exposure can damage the liver, kidneys, and develop sores when the skin is in contact with chloroform [112]. The National Institute for Occupational Safety and Health (NIOSH) set two limits for CHCl$_3$, recommended exposure limit of 2 ppm (for 60 min) based on risk evaluations using human or animal health effects data, and permissible exposure limit (PEL) of 50 ppm as carcinogen substance with targeted organs such liver, kidneys, and central nervous system [113]. Sharma et al. [25] developed a chemically synthesized copper/PANI nanocomposite for CHCl$_3$ detection in the range of (10–100 ppm). The sensitivity values (ΔR/R) for different CHCl$_3$ concentrations were found in the range of 1.5–3.5. However, at higher concentration, the observed (ΔR/R) appears to drop amazingly, which might be due to the low concentration of accessible metal clusters and bringing about the diffusion of chloroform molecules in the matrix. However, at low concentration ordinarily 10 ppm, (ΔR/R) decreases obviously on progressive exposures to chloroform suggestive of a competent interaction of analyte at dopant sites of the host polymer. This indicates that the unmistakably metal cluster incorporated conducting polymer can specifically and effectively be utilized as a chemical sensor [25].

Methanol (HCHO) is widely used in industry and in many household products (drugs, perfumes, colors, dyestuffs, antifreeze, etc). It is flammable, explosive, toxic and fatal to human beings even in modest concentrations. The US-CDC has recommended the short-term exposure limit of 800 ppm [114]. Athawale et al. [27] fabricated the PANI/Pd nanocomposite for methanol sensing. The experimental results revealed a very high response, by the order of
–104 magnitudes, for methanol (2000 ppm). In the case of PANI/Pd nanocomposite, Pd acts as a catalyst for reduction of imine nitrogen in PANI by methanol. It can also be seen that the PANI/Pd nanocomposite selectively monitored methanol with an identical magnitude of response in the mixture of VOCs, but took a longer response time [27]. Ma et al. [115] deposited PANI–TiO2 nanocomposite film on interdigitated carbon paste electrodes via a spin coating and immersion method for detection of trimethylamine N(CH3)3 at RT. This PANI–TiO2 nanocomposite film exhibited an appropriate gas sensitivity to N(CH3)3, with a 5.14 × 10−7 mol mL−1. It took about 180 s to reach three orders of magnitude for the value of gas-sensitivity, 450 s to reach five orders, and was selective to analogous gasses [115]. The sensing film exhibited reproducibility, stability, and easy recovery with high-purity N2 at RT.

Wang et al. [116] fabricated the sensor for VOCs gas sensing. The sensor was fabricated by using PANI intercalated MoO3 thin films, (PANI) x MoO3, on LaAlO3(100) (LAO) substrate. Typical response (signal (Rg/Ra)) of (PANI) x MoO3 thin film to selected VOCs with a concentration of 50 ppm with carrier N2 gas. An increase in the response signal Rg/Ra by 8.0% within 600 s (10 min) at 30 °C was observed upon exposure to formaldehyde (HCHO) vapor and an increase in Rg/Ra by 3.8% in response to acetaldehyde (CH3CHO) was also observed [116]. The experimental data clearly predict that (PANI)x MoO3 exhibits distinct sensitivity to formaldehyde (HCHO) and acetaldehyde(CH3CHO) vapors. While it was also observed that (PANI)x MoO3 with other polar gaseous species, (such as chloroform, methanol, and ethanol) used to show very weak sensitivity. Whereas, (PANI)x MoO3 sensor did not show any response to acetone, toluene, and xylene.

Geng et al. [117] fabricated the PANI/SnO2 nanocomposite synthesized by a hydrothermal method for detection of ethanol (C2H5OH) or acetone (CH3)2CO [117], XRD results demonstrated that the PANI/SnO2 nanocomposite had the same profile as pure SnO2, showing that the crystal structure of SnO2 was not altered by PANI. The gas detecting test for C2H5OH and (CH3)2CO was done at a fixed humidity of 60% and the operation temperatures were 30, 60 and 90 °C. In the gas detecting study, it was seen that the PANI/SnO2 nanocomposite had no gas sensitivity to ethanol or acetone when worked at 30 °C. However, when worked at 60 or 90 °C, it was sensitive to low concentration of ethanol and acetone. But the most extreme reaction was seen at 90 °C. The trec to C2H5OH and (CH3)2CO was 23–43 s and 16–20 s, individually, at 90 °C, and the trec was 16–28 s and 35–48 s, separately [117]. The possible sensing mechanism was thought to be related to the presence of p–n heterojunctions in the PANI/SnO2 nanocomposite.

Itoh et al. [118] reported the poly(N-methylaniline)/MoO3 ([PNMA]xMoO3) nanocomposite for making a VOC sensor, which was formed by an intercalation process to ion-exchange sodium ions for PNMA into MoO3 interlayers. This nanocomposite was made of grains (~500 nm). The (PNMA)xMoO3 nanocomposite was found to exhibit increasing resistive responses (~1–10 ppm) aldehydic gasses and these resistive responses indicate good reproducibility in its response, indicating that the can absorb and desorb aldehydic gasses within several minutes [118]. The sensitivity of the (PNMA)xMoO3 nanocomposite, whose organic component is a PANI derivative, to CH3CHO is nearly similar to HCHO. Itoh et al. [119] reported layered organic–inorganic nanocomposite films of molybdenum oxide (MoO3) with PANI, and poly(o-anisidine) (POANIS) formed by a modified intercalation process to probe the effect of aldehyde (HCHO and CH3CHO). However, (PANI)xMoO3 and (POANIS)xMoO3 thin films exhibited enhanced response (S = 68) as a function of resistance when exposed to HCHO and CH3CHO in the range of 25–400 ppb at 30 °C.

Yang & Liau reported the fabrication of nanostructured PANI films from polystyrene (PS)—PANI core–shell particles for the sensing of different dry gas flow, C2H5OH, HCl, and NH3. The experimental result clearly depicts that large surface area and porosity resulted in highly sensitive and fast response to different conditions, especially to dry gas flow and ethanol vapor [120]. Choudhury fabricated a PANI/Ag nanocomposite for the detection of ethanol and reported that during ethanol exposure in the presence of Ag NPs in the nanocomposite, the faster protonation—deprotonation of PANI took place. The sensor response of >2.0 and response time of 10–52 s for 2.5 mol% Ag was observed [28].

Lu et al. [121] fabricated a layer-by-layer PANI NPs–MWNT film of PANI NPs and MWNT onto interdigitated electrodes for the fabrication of stable chemiresistive sensors for methanol (CH3OH), toluene (C6H5CH3), and chloroform (CHCl3) detection with reproducible response upon chemical cycling. Double percolated conductive networks in PANI (1%)–MWNT (0.005%) nanocomposite resulted in both higher sensitivity (relative amplitude ~1.1%) and selectivity than other formulations, demonstrating a positive synergy [121]. Barkade et al. [23] reported the fabrication of PANI–Ag nanocomposite by an ultrasound assisted in situ mini-emulsion polymerization of ANI along with different concentrations of Ag NPs for ethanol (C2H5OH) sensing. Sensing measurements were performed at different C2H5OH vapor concentrations (75–200 ppm). It was observed that the nanocomposite showed a linear response (up to 100 ppm). Further, the change in resistance was found to be independent of Ag NP concentration. The increase in resistance of sensor on exposure to C2H5OH may arise due to the interaction of –OH groups of ethanol molecules and nitrogen of polyaniline, leading to electron delocalization and charge transport through the polymer chain. In comparison to pure PANI, the sensor response of PANI–Ag nanocomposite showed more stability as well as good reproducibility to C2H5OH vapors under the same condition. Steady linear response up to 2100 s was observed in the PANI–Ag film sensor to C2H5OH (100 ppm) which on further increase in time leads to saturation of the nanocomposite film. This can be attributed to decrease in available free volume for vapor permeability into the nanocomposite. The response time at 100–200 ppm C2H5OH of pure PANI sensor was recorded within 21–23 min, which decreased to 15–11, 13–10 and 8–6 min for the PANI–Ag nanocomposite sensor containing 0.5, 1.5 and 2 wt % of Ag, respectively [23].

Li et al. [122] fabricated PANI–MWNT (mass ratio 4:1) nanocomposite for hydrocarbon detection. This PANI–MWNT (mass ratio 4:1) nanocomposite sensor displayed a response to aromatic hydrocarbon vapors of various concentrations (200–1000 ppm) due to an increase in conductivity, and the maximum response (0.31%) was measured at 1000 ppm [122]. The increase in the conductivity of PANI after gas exposure has been attributed to physical interactions due to dipole–dipole interactions that uncoil the polymer chain and decrease the hopping distance for the charge carriers.

Triethyamine [N(CH2CH3)3] is also one of the volatile organic compounds (VOCs) with a strong ammonia smell, which is flammable, and combustible. It can cause pulmonary edema and even death. The PEL for N(CH2CH3)3 recommended by the US-OSHA is 25 ppm (8-h work shift). Li et al. [123] reported the PANI/Ag nanocomposite for detection of triethyamine and toluene. The suggested mechanism for the sensor response was based on the chemisorption and diffusion model. Li et al. [124] fabricated a triethyamine vapor sensor. The sensor was fabricated by using MWNTs–sodium polystyrene sulfonate (NaPSS) deposited on an interdigitated Au electrode decorated with a layer of positively charged poly (diethyl dimethyl ammonium chloride) by a self-assembly method. It was found that the composite exhibited a linear response to the vapor in the range of 0.5–8 ppm with the highest sensitivity of ~80%, which is much higher than that of
MWNTs and PANI separately, and an obvious synergetic effect was observed. In addition, the detection limit was as low as the ppb level, and reversible and relatively fast responses (tres~200 s and ~10 min for sensing and recovery, respectively) were observed. The sensing characteristics are highly related to the gas responses of PANI, and a sensing mechanism considering the interaction of MWNTs and PANI was proposed.

2.7. PANI-based nanocomposite for LPG detection

LPG is odorless and colorless and generates less emission than petroleum while burning. But, LPG is highly inflammable and must, therefore, be stored away from sources of ignition and thus their detection is very critical at RT. Joshi et al. [125] reported the use of n-CdSe/p-PANI nanocomposite for LPG sensing wherein the response was a result of the sensor’s modified depletion layer. Sensor response of ~70% for 0.08 vol% LPG was observed.

Dhawale et al. have carried out a lot of work focusing on PANI-based nanocomposite for LPG sensing at RT over the recent years. They fabricated a device with excellent stability, short response and recovery times, and showed significant selectivity towards LPG as compared to N2 and CO2. They too ascribed the sensor’s response to a change in the barrier potential of the heterojunction. PANI/TiO2; Sensor response of ~63% for 0.1 vol% LPG [126], n-CdS/p-PANI; it was ~80% for 1040 ppm LPG [127]. Dhawale et al. [126] also reported a LPG sensor based on a p-PANI/n-TiO2 heterojunction at RT. The fabrication of this heterojunction sensor was performed using electrochemically deposited polyaniline on chemically deposited TiO2 on a stainless steel substrate. The p-PANI/n-TiO2 sensor is known to show the increase in response from 15 to 63% with an increase in LPG concentration from 0.04 to 0.1 vol%. The sensor showed the maximum gas response of 63% at 0.1 vol%. At 0.12 vol% of LPG, the response decreased to 25%. It is also well revealed that the tres decreased from (200~140 s) when LPG concentration increased from 0.02 to 0.1 vol%. The reason for this may be due to the presence of sufficient gas molecules at the interface of the junction for reaction to occur.

Sen et al. [128] reported the detection of LPG by PANI/g-Fe2O3 nanocomposite at room temperature. Sensor response of 1.3 for 200 ppm LPG was observed. Based on the experimental investigation, the authors proposed a plausible mechanism for the detection of LPG. The authors suggested the sensing is the result of an increase in the depletion depth due to the adsorption of gas molecules at the depletion region of the p–n junction [128]. Bhanvase et al. [129] reported the fabrication of LPG sensors by using PANI and PANI/ZnMoO4 nanocomposite thin films with different loadings of ZnMoO4 (ZM) NPs. It was observed that in the PANI film, the sensor response increased up to 1200 ppm, however, in the case of PANI/ZM nanocomposite materials, it increased up to 1400 ppm. Sensor response for PANI and PANI/ZM nanocomposite sensors for LPG concentration (800~1800 ppm) was found to be 14.2%~35.6% and 20.6~45.8% respectively. The response and recovery time characteristics of the PANI/ZM nanocomposite sensor for an exposure of (1800 ppm) of LPG at RT were found to be 600 s and 840 s, respectively [129]. The graphene/PANI thin films sensor has a fast response and a good reproducibility for NH3 gas.

Patil and his co-worker reported the fabrication of a selective and sensitive LPG sensor based on electrosynapped nanofibers (NF) of PANI/ZnO nanocomposites [130]. In the case of PANI NF, sensitivity increased from 1.11% to 7.33% at 36 °C. But with an increase in temperature from 36 °C to 90 °C the sensitivity decreased from 7.33% to 1.25%. While the same was found in the case of PANI/ZnO NF, the sensitivity factor increased from 4.55% to 8.73% at 36 °C but as the temperature increased from 36 °C to 90 °C, the sensitivity decreased from 8.73% to 0.7% [130]. It was observed that with the addition of ZnO in polymer matrix resulted in an increase in the band gap by which caused the decrease in electrical conductivity, but the enhancement of the sensing response. The tres was found to be 100 s for PANI/ZnO and 110 s for pure PANI. The trec was long i.e. 185 s for PANI/ZnO and 195 s for pure PANI at (1000 ppm concentration) for LPG [91]. There are different methods used by different workers to form PANI nanofiber composites [131~135]. Khened et al. [136] reported Poly(aniline)/Barium zirconate (BaZrO3) composites for LPG sensing. The composite was prepared by in situ polymerization with 10, 20, 30, 40, 50 wt% of BaZrO3 in polyaniline 1000~40000 ppm. The LPG sensitivity of about 1% at 40,000 ppm was obtained for 50 wt% BaZrO3 in PANI. Joshi et al. [137] reported on a n-CdTe/p-polyaniline heterojunction-based room temperature LPG sensor. This sensor showed the maximum response of ~67.7% to 0.14 vol% of LPG at RT. The sensor response increased from 30% to 67.7% with increasing the LPG concentration from 0.02 to 0.14 vol%. At 0.16 vol%, it decreased to 50%. The reason may be due to the recombination of carriers. The tres was found to be in the range of 80 and 300 s depending on the LPG concentration, and the trec was about 600 s.

Sen et al. [128] reported Poly(aniline)/ferric oxide (PANI/-Fe2O3) NC films for LPG sensing at RT. The PANI/-Fe2O3 NC films were studied for their response to LPG at (50~200 ppm) LPG concentrations. The maximum response for PANI/-Fe2O3 (3 wt%) NC films for 50 ppm LPG was reported to be 0.5% with a response time of 60 s. The sensing mechanism pertains to a change in the depletion region of the p–n junction formed between PANI and -Fe2O3 as a result of electronic charge transfer between the gas molecules and the sensor. Shinde et al. [138] reported the fabrication of a PANI/Cu2ZnSnS4 (CZTS) thin film based heterostructure as a room temperature LPG sensor. The maximum gas response of 44% was observed at 0.06 vol% of LPG for this sensor. The LPG response decreased from 44% to 12% at the relative humidity of 90%. The PANI/CZTS heterojunction showed good stability and fast response and recovery time periods.

2.8. PANI-based nanocomposite for CO2 detection

Carbon dioxide (CO2) is a colorless, odorless, noncombustible gas. It is broadly realized that CO2 is the essential greenhouse gas discharged through human exercises. The rise in the level of the CO2 concentration in the air since the industrial revolution has assumed a basic part in a global warming alteration and atmosphere change. The US-OSHA exposure limits of CO2 are 10,000 ppm [8-h Time-weighted average (TWA)] and 30,000 ppm [15-min short-term exposure limit (STEL)]. The effect of a global warming alteration has motivated numerous research on the detection, capture and storage of CO2. Nemade and Waghule fabricated thick films of chemically synthesized cerium (Ce) doped PANI using screen-printing on a glass substrate for CO2 gas sensing at RT [139]. It was shown that the sensing response decreased with an increase in the molar concentration of CeO2. This shows that lower concentrations of CeO2 resulted in improved sensing responses. The resistance of all Ce-doped PANI films increased with an increase in CO2 gas concentration. The decreased sensing response was observed with increasing concentration of Ce in PANI. It has been suggested that O2 ions readily form weak bonds with π-electron clouds of PANI. The O2 ions adsorb onto the surface of the material which removes electrons from the bulk, subsequently increasing the barrier height and the resistivity [139].

Nimkar et al. [140] fabricated the PANI/TiO2 nanocomposite thin film based chemiresistive sensor for detection of CO2 gas in atmosphere. Sensor response for CO2 concentration (1000 ppm) was
found to be 5% at 35 °C and it decreased from 5 to 1% with increasing temperature from 35 °C to 60 °C. The response and recovery time characteristics of PANI/TiO2 nanocomposite sensor for an exposure of 1000 ppm of CO2 at RT was found to be 70 s and 80 s, respectively. Therefore, it is concluded that the PANI/TiO2 nanocomposite is a good chemiresistor sensor for CO2 gas sensing at RT [140].

2.9. PANI-based nanocomposite for CO detection

Carbon monoxide (CO) is a colorless, odorless, hazardous, and poisonous gas that is produced from industrial processes and is also present in human breath [141]. The PEL for CO recommended by US-OSHA is 35 ppm (10-h ceiling limit), whereas the US-NIOSH suggests a limit of 50 ppm (8-h ceiling limit) [142]. Thus there is a need for developing sensors that can detect carbon monoxide [143]. Mishra et al. [144] reported the rapid and selective detection of CO at a ppb level using vacuum-deposited PANI–Fe:Al (80:20) nanocomposite thin films. Using these sensors, CO could be detected in the range 0.006–0.3 ppm at room temperature. These sensors showed the very high sensitivity of the order of 400–600, and response times of 10 s at RT. For CO sensing (7.5–1000 ppm), Densakulprasert et al. [145] measured the electrical conductivity of PANI-zeolite nanocomposites as a function of precursor concentration, pore size, and the ion exchange capacity of zeolite. The highest electrical conductivities and sensitivities were obtained with the 13X zeolite, followed by the Y zeolite, and the AIMCM41 zeolite.

Sen et al. [146] fabricated the PANI/Co3O4 nanocomposites for their sensitivity towards CO gas at RT. The synthesis of Co3O4 NPs was performed by using ultrasound assisted co-precipitation method and then incorporated into the PANI matrix. The PANI/Co3O4 nanocomposite sensors were found to be highly selective to CO gas at RT. A significantly high response of 0.81 was obtained for 75 ppm CO concentration with a response time of 40 s [146].

2.10. PANI-based nanocomposite for sulfur dioxide (SO2) detection

Sulfur dioxide (SO2) is a poisonous gas with the US-OHSA PEL exposure limit of 5 ppm [147]. It attacks the human respiratory system [148] and is the major reason for acid rain [149]. Thus, its monitoring is critically required. There are very few reports in the literature about sulfur dioxide sensing by individual PANI [150–155] and WO3 [156–159] based sensing devices, but lack the essential parameters required for reliable SO2 monitoring. Betty’s team systematically studied the fabrication of nanocrystalline SnO2–PANI heterostructure sensors for sensing trace amounts of toxic gases (2 ppm SO2 and 50 ppb NO2) at RT (25 °C). Stability studies carried out for these heterostructure sensors and obtained the same response over 3 months [160].

Chaudhary and Kaur [161] reported the fabrication of PANI–WO3 hybrid nanocomposites with a honeycomb type morphology was synthesized by in situ one-pot chemical oxidative method for sensing of SO2. The sensor response of PANI–WO3 was found to be ~10.6%, which is much greater as compared to pure PANI (~4%) and negligible for WO3 for 10 ppm SO2 at RT. In order to test the authenticity of PANI–WO3 hybrid nanocomposite sensor studied was performed at 6 different concentration of SO2. The results showed that sensor response was ~4.3%, ~10.6%, ~24%, ~36%, ~51.5% and ~69.4% for 5 ppm, 10 ppm, 25 ppm, 40 ppm, 60 ppm and 80 ppm of SO2, respectively at RT. Selectivity study was also performed by the authors, for which different toxic gases were used, such as CH3OH, C2H5OH, C2H4, and H2 (10 ppm), at RT were used. The sensor response was found at RT to be ~10.6%, ~2%, ~0.5%, ~4% and ~1.5% for SO2, C2H5OH, C2H4OH, NH3 and H2S (10 ppm), respectively. The stability and reproducibility of the sensing device were studied for four consecutive weeks. It was observed that sensor response was 10.5%, 9.9%, 9.7% and 9.68% for 1, 2, 3 and 4 weeks respectively, for 10 ppm SO2 at RT. This sensor works well at RT, which reduces the cost of power and the need for complex circuitry. It also showed high selectivity, stability and reproducibility at RT.

2.11. PANI-based nanocomposite for detection of explosives and chemical warfare agents

At present, as the terrible activities are of high frequency, the detection of explosives and chemical warfare agents (CWAs) attracts an increasing attention in many fields and is becoming a hot topic for research.

2.11.1. Trinitrotoluene (TNT) C7H2N3O6 detection

TNT (C7H5N3O6) occurs as yellow, needle-like crystals and is used as an explosive. OSHA PEL for 2,4,6-trinitrotoluene (TNT) was 0.5 mg/m3 as an 8-h TWA, with a skin notation. Gang et al. established a prominent analytical platform for electrochemical detecting of nitroaromatic explosive compounds, such as 2,4,6-trinitrotoluene (TNT) by utilizing PANI and PANI/TiO2 nanocomposites at RT [162]. The TiO2 nanotubes (NTs) array was assembled through electrochemical oxidation of pure titanium in a fluoroine ion-containing ethylene glycol water solution followed by annealing at 450 °C in air. PANI was obtained by electrochemical polymerization from an ANI and H2SO4 solution. TiO2 NTs on the pure Ti sheet were coated with PANI to form a PANI/TiO2 NTs hybrid nanocomposite. The process for fabricating the PANI/TiO2 hybrid nanocomposite is similar to that for synthesizing PANI on copper. The 25% of mass content of PANI was used for synthesis of the PANI/TiO2 nanocomposite. The results clearly depict that the TiO2 NTs sorbs more TNT (6.90 ng mg−1) than the pure titanium (0.410 ng mg−1). The PANI/TiO2 nanocomposite showed the highest sorption of TNT, which is 9.78 ng mg−1.

2.11.2. Cyanide detection

Cyanide agents are very dangerous compounds that are called “blood agents” and used as chemical warfare agents. So, we would like to detect these compounds in low concentrations for human safety. Hosseini reported the synthesis of polystyrene-graft-polyaniline (PS-g-PANI), by adding solution of APS and p-toluene-sulfonic acid in water [163]. PS-g-PANI was also exposed to some cyanide compounds such as hydrocyanic acid (HCN), ethanedinitrile (C2N2O), cyanogen chloride (CNCI), and cyanogen bromide (CNBr). A different concentration of blood agents at 50, 100, and 150 ppm and exposed them on PS-g-PANI for 2 min. The resistivity of PS-g-PANI decreased upon exposure to tested samples. It was observed that the increase in the concentration of cyanide compounds increased the sample conductivity.

2.11.3. Arsin (AsH3) detection

Arsine (AsH3) was proposed as a possible chemical warfare weapon before World War II. AsH3 gas is colorless, almost odorless, and 2.5 times denser than air, as required for a blanketing effect sought in chemical warfare. AsH3 is a very toxic gas used in the semiconductor industry with a permissible exposure limit (PEL) of 50 ppb. Virji et al. reported the fabrication of a Cu(II) bromide/PANI nanofiber composite sensor for AsH3 sensing at RT [164]. It was observed that the composite showed a greater response as compared to the other materials used. It was found that the copper(II) bromide/PANI nanofiber composite sensor proved useful in detecting toxic gasses that unmodified PANI nanofibers but is unable to detect AsH3. The AsH3 sensors showed...
large electrical responses under low concentrations, the use of inexpensive and inert materials and a synthetic method that is easily scalable.

2.11.4. Dimethyl-methyl-phosphonate (DMMP) CH₃PO(OCH₃)₂ detection

Sarin is known to be one of the strongest nerve gas agents. Sarin is widely used in chemical warfare, producing disastrous effects within seconds after inhalation. To immediately realize Sarin’s rapid action and deadliness, the fabrication of a fast, accurate gas detection technique is paramount [165]. Dimethyl-methyl-phosphonate (DMMP) is known to a typical stimulant of Sarin which is well used by many scientists in Sarin gas-related experiments.

Chang et al. [166] worked on DMMP-sensing based on composites of MWCNTs and PANI, but their sensor was reported to show a response of 1% at 332 ppm DMMP. But the study showed that PANI resulted in a reduction of the response time whereas any single material of SWCNTs, MWCNTs, and PANI had a limited response. Yoo et al. [167] reported the composite sensor composed of SWCNTs and PANI, in response to the nerve agent simulant gas, DMMP, a typical Sarin simulant. Yoo and his co-worker fabricated the SWCNT-PANI composite by dispersing the mixed solution of SWCNTs and PANI on the oxidized Si substrate between Pd electrodes. During this process, large amounts of SWCNT networks and PANI strands were present between the two electrodes, but for simplicity, only a single PANI strand winding around one SWCNT is shown in Fig. 13a by authors. TEM images of the SWCNT-PANI composite provided in the inset of Fig. 13a. Fig. 13b shows TEM images of the SWCNT-PANI composite, while Fig. 13c shows TEM images at high magnification focusing on the single strand of SWCNT-PANI composite. Thus this results clearly confirms that PANI strand wrapped around the SWCNT exhibits high-quality composites with good uniformity. The authors have used the sensor for sensing DMMP gas at RT by monitoring the change in resistance of SWCNT-PANI composite. (b and c) TEM images of SWCNT-PANI composite. [Reprinted with permission from Ref. [167]. Copyright 2015 Elsevier].

DMMP gas causes increase in resistance of the SWCNT-PANI composite film after interaction because SWCNTs and PANI have majority carrier (hole) densities which get decreased by the transferred electrons.

The S and t_{res} were 27.1% and 5.5 s, respectively, at 10 ppm DMMP, representing a significant improvement over the pure SWCNT network sensors. The SWCNT–PANI composite sensor response was examined at various DMMP concentrations. The response clearly increases linearly with increasing DMMP concentration, as summarized in Fig. 14b. The linear correlation between SWCNT–PANI sensor response and DMMP concentration emerges from the recurrence of DMMP adsorption are mostly proportional to its concentration. The results clearly demonstrated a very high response, rapid response time, high reproducibility, and room-temperature operability ideal DMMP sensors.

Yuan and Chang reported MWNNTs-Polyaniline (PANI) sensor for detection of CH₃OH, CHCl₃, CH₂Cl₂ and simulation chemical warfare agent (DMMP as a nerve agent) [168]. Chemoresistive multi-layer sensor was fabricated by drop-coating polyaniline (PANI) solution on chemically modify MWNNTs. It was observed that upon exposure to different chemical vapors, the sensing film swells reversibility and caused changes in resistance after exposure to CH₃OH (2122 ppm), CHCl₃ (2238 ppm), CH₂Cl₂ (481 ppm) DMMP (332 ppm). MWNNTs/PANI sensing films resistivity toward DMMP, CH₂Cl₂, CH₃OH and CHCl₃ are −21−22.02% of magnitude, respectively. The sensitivity of the MWNNTs/PANI sensing films drastically increased by 8−22% of exposure to DMMP and CH₂Cl₂ vapors, and 0.4−0.9% of exposure to CHCl₃ and CH₃OH within 300 s. While when the sensing film is transferred back to dry air, the electrical resistance returned to the original value rapidly, demonstrating a good restoring performance. The MWNNTs-Polyaniline (PANI) sensor also shows better resistance reproducibility and stability after four cycles of exposure to solvent vapors and a dry air.

2.11.5. Phosgene (COCl₂) detection

Phosgene (COCl₂) is a colorless, highly toxic industrial chemical that has a low permissible exposure limit (PEL) of 0.1 ppm and an immediate danger to health and life (IDLH) limit of 2 ppm [169]. Presently it is used in the factory to make dyestuffs, polyurethane resins, plastics and pesticides and was used as a chemical weapon.

Fig. 13. (a) A schematic of an SWCNT–polyaniline composite sensor on an oxidized Si substrate with Pd electrodes. The inset shows an SEM image of the SWCNT–polyaniline composite. (b and c) TEM images of SWCNTs–polyaniline composite. [Reprinted with permission from Ref. [167]. Copyright 2015 Elsevier].
during World War I. During Inhalation, COCl₂ reacts with water in the lungs to form HCl and CO, which causes pulmonary edema, bronchial pneumonia and lung abscesses. Virji et al. [170] reported the fabrication of amine–PANI nanofiber composite materials in aqueous solution by addition of the amine solution to an aqueous suspension of PANI nanofibers. The different amines and amine salts used are ethylenediamine, ethylenediamine dihydrochloride, phenylenediamine, phenylenediamine dihydrochloride, and metanilic acid used in the synthesis of amine-polyaniline nanofiber composite materials. Virji et al. drew a conclusion that composites of PANI nanofibers with amines respond well to phosgene at concentrations 0.1 and 2 ppm at 22 °C and 50% RH. Amines are known to react with COCl₂ in a nucleophilic substitution reaction to form carbamoyl chlorides (R₂NCOCl) which can be readily dehydrohalogenated to form isocyanates (R₂N=C=O) [171]. In this reaction, HCl is formed, which can dope the PANI converting it from the emeraldine base oxidation state to the emeraldine salt oxidation state. This resulted in two orders of magnitude increase in conductivity.

3. Conclusions

PANI-based sensors, which convert a chemical interaction into an electrical signal, covering a wide range of applications, have effectively been demonstrated as proficient sensors for monitoring organic and inorganic compounds. In this review, we have explored current progress in the development of PANI hybrid nanocomposites for gas/vapor sensors for environmental monitoring at RT. The basic principles, sensor parameter and properties of PANI-based nanocomposites and their use in various gas/vapor sensor applications are analyzed and discussed in great detail. Nanostructured PANIs exhibit excellent sensing behavior because of their desired functionality and conductivity. The review has revealed the structural versatility of these nanocomposites as sensitive chemical sensors, with additional advantages of high selectivity, fast response and recovery time and great stability.

4. Challenges and future prospects

The response and recovery times and the sensitivity have encountered magnificent enhancements with an impressive progress in the nanotechnology over the past decades. As we know that selectivity is still a major challenge for gas sensing. Detecting target species in a complex environment remains a troublesome assignment, and is impeding the extensive application of conducting polymer-based sensors. Cross sensitivity means sensors exhibit homogeneous responses to distinctive types of gasses, and this character may result in false detecting. It is also observed that nanostructured based sensors had relatively poor sensitivity and moderate response time because of the functional properties which are not yet fully understood [12]. A clear understanding of these properties will shed light on controlled synthesis of new nanostructured conducting polymers that fulfill the aforementioned requirements [172].

It is noted that different parameters, such as shape and size of inorganic nanostructures, porosity, inter-phase interaction, surface and interfacial energy, catalysts activity, and chemical reactivity control the response of the gas sensors. These parameters also rely on the type and concentration of inorganic additives. Apart from those, the ratio of the organic and inorganic materials is very crucial and needs attentive optimization to accomplish great detection sensitivity.

One of the critical difficulties we are facing with is the non-repeatability of device fabrication. The hypothesis can demonstrate a heading for practice. However, till now, the gas/vapor sensing mechanism of nanomaterials is not clear, and quantitative estimation is practically difficult. A great deal of consideration is yet excessively paid to the choice of detecting materials to enhance the 3S concept i.e., selectivity, sensitivity and stability for the improvement of gas sensing devices. Technique towards free-standing PANI nanofibers by enhancing the mechanical properties is another approach for upgrading the usability of PANI nanofibers for gas sensing application. In literature, we have found no or very limited sensing research on heavy explosive molecules like, trinitrotoluene (TNT), Dinitrotoluene (DNT), pentaerythritol tetranitrate (PETN), hexahydro-1,3,5-triazine (RDX) and chemical warfare agents like phosgene, chlorine, DMMP, arsine etc. Thus further research needs to be conducted. The future of PANI-based nanocomposite gas/vapor sensors is bright and continued progress in this field will overcome the current challenges, creating a novel class of gas sensors with low power consumption, low cost, superior sensitivity, excellent selectivity, miniaturization, and long-term stability for a wide range of applications in different ways such as industrial emission control, control of nuclear power plants, household security, vehicle emission control, and environmental monitoring.
Conflicts of interest

The authors declare no competing financial interests.

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