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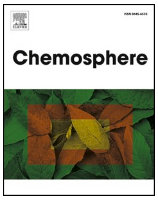

Advanced polymeric/inorganic nanohybrids: An integrated platform for gas sensing applications

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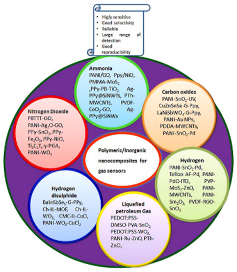
HIGHLIGHTS

- Effects of toxic gases on human health have been described.
- Polymer/inorganic nanohybrids based sensors have been discussed for gas sensing.
- Basic sensing mechanism of gas sensors has been reviewed.

GRAPHICAL ABSTRACT



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ABSTRACT

Rapid industrial development, vehicles, domestic activities and mishandling of garbage are the main sources of pollutants, which are destroying the atmosphere. There is a need to continuously monitor these pollutants for the safety of the environment and human beings. Conventional instruments for monitoring of toxic gases are expensive, bigger in size and time-consuming. Hybrid materials containing organic and inorganic components are considered potential candidates for diverse applications, including gas sensing. Gas sensors convert the information regarding the analyte into signals. Various polymeric/inorganic nanohybrids have been used for the sensing of toxic gases. Composites of different polymeric materials like polyaniline (PANI), poly (4-styrene sulfonate) (PSS), poly (3,4-ethylene dioxythiophene) (PEDOT), etc. with various metal/metal oxide nanoparticles have been reported as sensing materials for gas sensors because of their unique redox features, conductivity and facile operation at room temperature. Polymeric nanohybrids showed better performance because of the larger surface area of nanohybrids and the synergistic effect between polymeric and inorganic materials. This review article focuses on the recent developments of emerging polymeric/inorganic nanohybrids for sensing various toxic gases including ammonia, hydrogen, nitrogen dioxide, carbon oxides and liquefied petroleum gas. Advantages, disadvantages, operating conditions and prospects of hybrid composites have also been discussed.

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1. Introduction

Gas sensors have attained attention in research fields and industrial areas because air contains various toxic gases that are hazardous for human health (Akram et al., 2021). The toxic gases may cause asthma, skin burning, dizziness, drowsiness, vomiting, nausea, cancer, lung issues, hypoxia, weight loss etc. (Dhall et al., 2021). Every gas has threshold limit value (TLV) which represents the concentration of respective toxic gas in atmosphere that may be breathed by most people with no bad effects. It is typically presented in parts per million (Fig. 1). For safety of living beings including animals, plants and humans, the sensing of toxic gases in environment is most important. Gases are emitted from different sources and few gases may react to form new compounds in atmosphere (Cunha et al., 2015). The continuous release of different gases such as ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2) hydrogen sulfide (H_2S), nitrogen dioxide (NO_2) and volatile compounds creates various issues including ozone depletion, acid rain, sick house syndrome and global warming. There are two main sources (Natural and man-made) of introduction of toxic gases in environment. The natural sources include volcanic eruption, cloud lightning, livestock and natural wild fire in forests. While man-made sources include smoke of aeroplanes, factories, automobiles, ships, coal burning, agriculture and domestic activities (see Fig. 2). There are several techniques including GC/MS and optical spectroscopies which are used to detect gases but they have various drawbacks like time consuming, expensive, bigger instrument and difficult to use in field. To control air pollution, there is a need to develop sensors to detect these gases quickly. By using various sensing materials and different transduction elements, different gas sensors have been developed.

Hybrid nanomaterials are unique conjugates of inorganic and organic materials (Tabish et al., 2021). In comparison of single component, the hybrid materials contain versatile functionalities along with increased chemical and physical features. Advance nanostructures based on organic/inorganic composites are significant for innovations in various fields (Nadeem et al., 2021; Yasin et al., 2020) particularly in gas sensing applications. Hybrids contain increased conductivity, porosity, catalytic activity, optical and electrical potential (Ibraheem et al., 2020; Nadeem et al., 2020).

Miscible polymeric composites are of great concern but generally polymers are immiscible in absence of specific type of interactions with them. Polymeric hybrids may possess the weak bonding interactions like hydrogen bonds and van der waals forces between organic and inorganic parts, while few organic/inorganic hybrids contain strong chemical bonds at the interface. These interactions are dependent on size, dispersion form, shape and size distribution of nanoparticles (Adnan et al., 2018). Nanohybrids have potential to detect gases even at ppm concentration. Previously, semiconductor gas sensors (ZnO, SnO_2, NiO, CuO) have been reported for their gas sensing applications and a

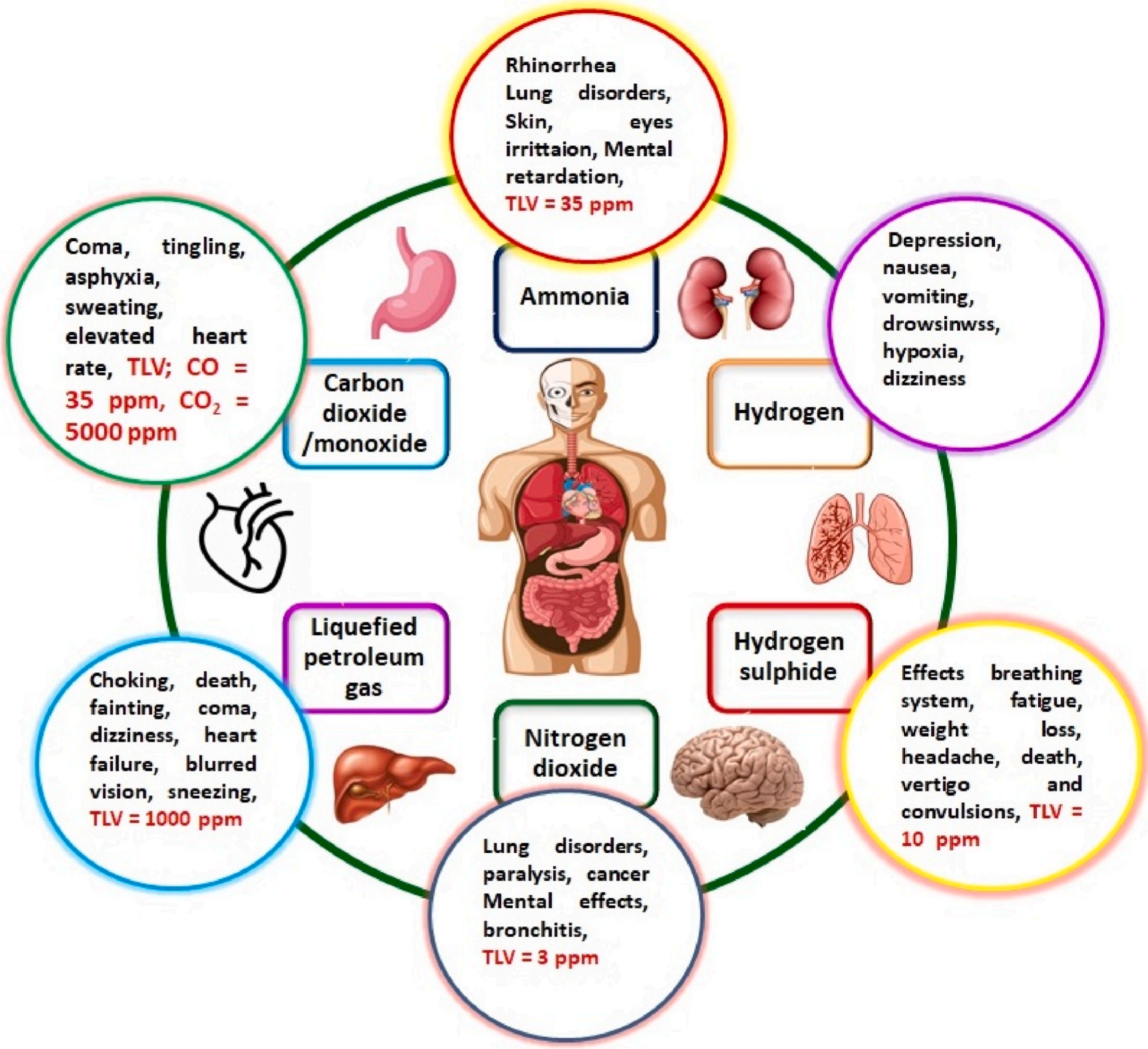

Fig. 1. General representation of health effects of toxic gases on human being. TLV represents threshold limit value.

significant attention was paid to them because of their good sensitivity, cost effectiveness and good capability in detecting wide range of toxic gases (Manjakkal et al., 2020). However, semiconductor based sensors possess lower selectivity, surface defects, poor adsorption potential and lower anti-corrosive properties (Seekaew et al., 2019). Synthesis of nanohybrids opened new dimensions for the researchers to achieve great selectivity with enhanced sensitivity. Conducting polymers including poly (3,4-ethylenedioxythiophene) (PEDOT), polyacetylene (PA), polythiophene (PT), poly (phenylene vinylene) (PPV), polyaniline (PANI) and polypyrrole (PPy) are sensitive materials and they have shown excellent potential in gas sensors because of their conductivity changes upon exposure of gas molecules (Ibanez et al., 2018). These polymers have benefits of cost effectiveness, high functionalities, great stability, short response time, great recovery, facile synthesis and high surface area. Various disadvantages including poor sensitivity, slow response, poor selectivity and poor recovery are also limiting factors associated with their gas sensing performance. Nanohybrids of polymer with inorganic nanomaterials overcome the defects of polymers/metal oxides, enhance their stability, sensitivity and response. Composites of polymers with inorganic nanomaterials including metal oxides, metal oxide semiconductor and other materials are famous class of sensing materials (Farea et al., 2021) with enhanced features like increased sensitivity, great surface area, lowering of sensor working environment and detection of wide range of gases (Nguyen et al., 2013). Different methods like physical, chemical and electrochemical techniques have been employed previously for the synthesis of polymeric/inorganic nanohybrids for gas sensing. In this review, we have focused on synthesis and applications of different polymer/inorganic nanohybrids for sensing of various harmful gases including hydrogen, ammonia, hydrogen sulfide, carbon dioxide, carbon monoxide, nitrogen dioxide and LPG (liquefied petroleum gas). Besides, efforts have been made to report concentration of analyte, response time, operating temperature, recovery time and advantages and disadvantages of nanohybrid materials in gas sensing process.

2. Polymeric nanohybrids for gas sensors

Previously, metal oxide based semiconductors have been used to sense gases but they need higher operating temperatures. Since 1980's, polymers are used as active-layer of gas sensor (Miasik et al., 1986). Composite of polymeric materials with metal oxides or other inorganic materials can enhance the selectivity and different sensing features due to the synergistic and geometrical effects (Hangarter et al., 2013; Miller et al., 2014). Polymeric materials possess larger surface area and good electrical conductance. When the gas molecules either electron acceptor or donor get adsorbed on the surface of polymer induces change in carrier concentration around polymer, and therefore, variation in resistance occurs (Varghese et al., 2015). Large surface area of polymeric materials enable gas molecules to adsorb in a better way. Various metals based gas sensors have been reported previously for gas sensing (Sharma and Kim, 2018; Zhang et al., 2019b) but efficacy of these devices was improved by synthesizing the nanohybrids of inorganic materials with polymers (Muthusamy et al., 2021; Sonwane et al., 2019). Various inorganic metal oxides may perform as catalyst to decompose gases in free radicals and facilitate their combination with oxygen having functional moieties on polymeric surfaces, and hence, showing great response towards such gases (Karaduman et al., 2017).

2.1. Basic sensing mechanism

Gas sensors consist of the sensing material and these are devices which have the ability to sense toxic gases. Gas sensors are classified on

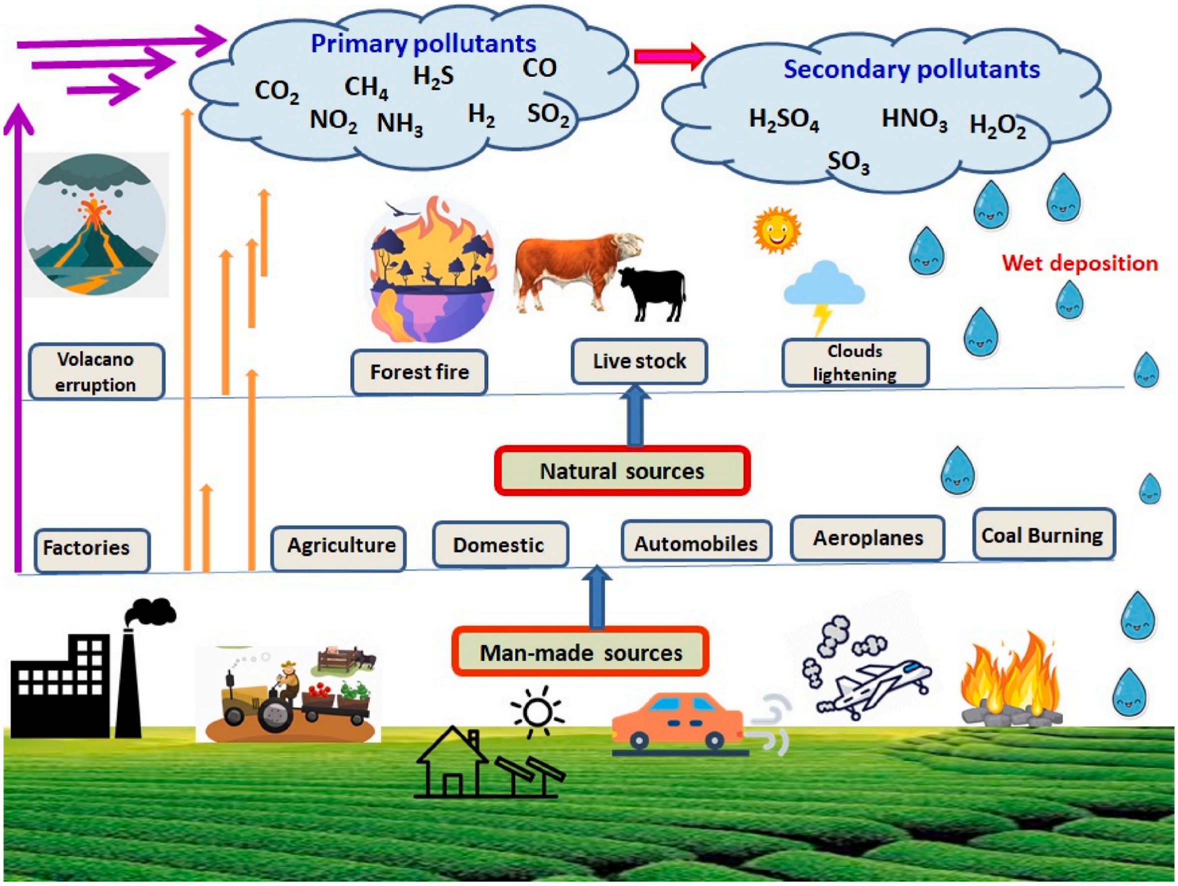

Fig. 2. Representation of Natural and man-made sources responsible for introduction of toxic gases in environment.

the basis of their reaction with atmospheric gases. Different known types of gas sensors are quartz-crystal microbalance, field effect transistors, chemiresistors, etc. From all sensors, chemiresistive sensors are famous because of the facile and cheap synthesis process, easy operation and small in size (Joshi et al., 2018). This sensor can determine the change in resistance of sensing material upon exposure of the target gas. Change in electrical resistance of sensing material occurs after interaction with gases (Banica, 2012). These sensors can be used for monitoring of air quality index, sensing of toxic gases, medical diagnostic purpose and also in food processing because of cost effectiveness, facile operation and good compatibility with other devices (Mirzaei et al., 2016).

The main mechanism involves the direct charge transfer phenomena between polymeric surface and the gas molecule. Inorganic materials (metals etc.) show catalytic potential upon contact with the various gases and while in coordination with polymeric materials, the sensing capacity of nanohybrid is significantly enhanced. During recent years, different groups have synthesized polymer and inorganic nanomaterials based nanohybids for sensing of toxic gases (Gaikwad et al., 2017). Large surface area and provision of many active sites on nanohybrid enable the gas molecules to adsorb on surface of nanohybrid in good manner. In nanohybrids, the polymeric materials prevent the agglomeration of inorganic materials (metal oxides), while metal oxides also play a role in the prevention of polymer fossilization. Different adsorbed oxygen species are formed upon acquisition of electrons by the atmospheric oxygen from oxides conduction band. Depletion layer forms on metal oxides surface which leads to an increase in resistance. After exposure of sensor with measured gas, the electrons from conduction band are captured by target gas and reacts with O_2 molecules on sensor surface. This phenomena leads to a decrease in conductance of sensor. Inorganic metal oxides are n-type semiconductors and polymeric materials are p-type semiconductors, thus formation of p-n junction during the process can increase the conductivity and this can be explained through p-n heterostructure theory. The fermi energy level of metal oxides is low in comparison of polymers, thereof, polymer accepts electrons from metal oxide surface which leads to the same fermi energy level of both materials. At this point, the electrons number onto the surface and at the interface of metal oxide decreases, the potential barrier enhances, broadening of depletion layer occurs and eventually sensor resistance changes significantly. The understanding of sensing mechanism is very important to enhance the selectivity and sensitivity of gas sensors. Conductance of n-type semiconductor increases with reducing analyte while it decreases with oxidizing analyte (Tricoli et al., 2010) and vice versa effects are observed with p-type semiconductor where holes are majority of charge carriers. The conductivity increases in the presence of oxidizing gas as number of holes increases while it decreases when reducing gas is incorporated as the concentration of hole charge carrier decreases (Pandey and Nanda, 2013).

2.1.1. Gas-sensing performance parameters

The detection limit, operational temperature, response time, recovery time, stability, sensitivity, repeatability and selectivity are various parameters to determine the performance of gas sensor (Yang et al., 2013). Ratio of resistance when exposed to background and target gas environments represents the sensor response towards reducing gases. Response towards oxidizing gases is represented as ratio of resistance when exposed to target gas and background environment. Sensor response is calculated through the following equations:

$$S = \frac{R_o}{R_g} \qquad (\text{reducing environment}) \tag{1}$$

$$S = \frac{R_g}{R_o} \qquad (\text{oxidizing environment}) \tag{2}$$

R_o and R_g represent the resistances of sensor in background gas and target gas, respectively while S represents the sensor response. On the basis of electrical response, various approaches are employed for determining the gas sensor sensitivity. Sensitivity is basically defined as a change in response to certain target gas concentration. The capability of sensor to respond in selective manner, in the presence of numerous materials, is called selectivity. Selectivity feature of a sensor tells that whether sensor can respond selectively to an analyte. Repeatability tells us that how many times sensor result will remain constant when tested under similar environment. Response and recovery time represents the time required to reach 90% of total change in resistance during exposure and removal of gas, respectively. Limit of detection or LOD represents the lowest gas concentration that can be detected via a gas sensor. The temperature at which a gas sensor shows maximum sensitivity is known as a working temperature (Kang et al., 2010).

3. Gas sensing applications of polymeric/inorganic based nanohybrids

Gas sensing performance of different polymeric/inorganic nanohybrids for sensing of different toxic gases including hydrogen, ammonia, hydrogen sulphide, nitrogen dioxide and carbon oxides has been reported in detail in this section (Fig. 3).

3.1. Sensing of ammonia

Ammonia (NH_3) is a toxic, colourless, and harmful gas, which needs to be detected in medical, industrial and living environments (H.-Y. Li et al., 2020b; Z. Li et al., 2020c). It is an atmospherically, industrially and biologically key inorganic compound which can be extensively used in many industries including fertilizer, household cleaners, petroleum, fire power plants, rubber, organic compounds, food processing, medicines, automobile, etc. (Abun et al., 2020; Das and Roy, 2021). However, in these applications, there is a high possibility of ammonia release into the atmosphere, causing severe air pollution. Smaller concentrations of ammonia can exert multiple effects on human health including irritation on eyes, skin and upper respiratory tract along with nausea, dizziness and fatigue (Diana et al., 2018; Li et al., 2020b). On the other hand, higher concentrations of ammonia can cause serious concerns such as cardiac arrest and damage to the birthing system. According to U.S. Occupational Safety and Health Administration (OSHA), the permissible time-exposure limit of ammonia gas is 15 min for 35 ppm and 8 h in case of 25 ppm, after which it becomes hazardous to the human health (Das and Roy, 2021; Fan et al., 2020). Moreover, ammonia is an important component of metabolism and, therefore, it is a typical biomarker of urea imbalance caused by renal disease or H. pylori-induced gastric infection (Tai et al., 2020). Thus, the detection of ammonia gas in exhaled human breath is a unique way of diagnosing kidney diseases. In short, highly sensitive, instant, accurate and effective ammonia gas sensing at room temperature has become an important factor for health care, environmental monitoring and industrial safety.

Wu and his colleagues reported the fabrication and ammonia sensing characteristics of polyaniline (PANI) based nanohybrid sensor modified with graphene (G) as an additive on porous polyvinylidene fluoride (PVDF) substrate (Q. Wu et al., 2021). In-situ polymerization method has been used to prepare the G-PANI-PVDF film (Fig. 4a). In short, G-PVDF film was produced by dipping the PVDF substrate in the graphene-ethanol mixture. G-PVDF films were then immersed in a mixture of aniline and HCl under magnetic stirring followed by the immersion in the mixture of ammonium peroxydisulfate (APS) and HCl. The polymerization of aniline on G-PVDF films was identified by the change in colour from grey-white to dark green of the films. In the end, silver electrodes were produced by screen printing on the prepared G-PANI-PVDF films. The ammonia sensing properties of the synthesized flexible sensor was analysed by self-made testing system (Fig. 4b), which can record the data points and transfer the numerical values to the computer through Bluetooth. The results showed that the response and recovery time of PANI based sensor decreased from 150 s to 46 s and from 300 s to 198 s, respectively, by incorporating graphene. The lower

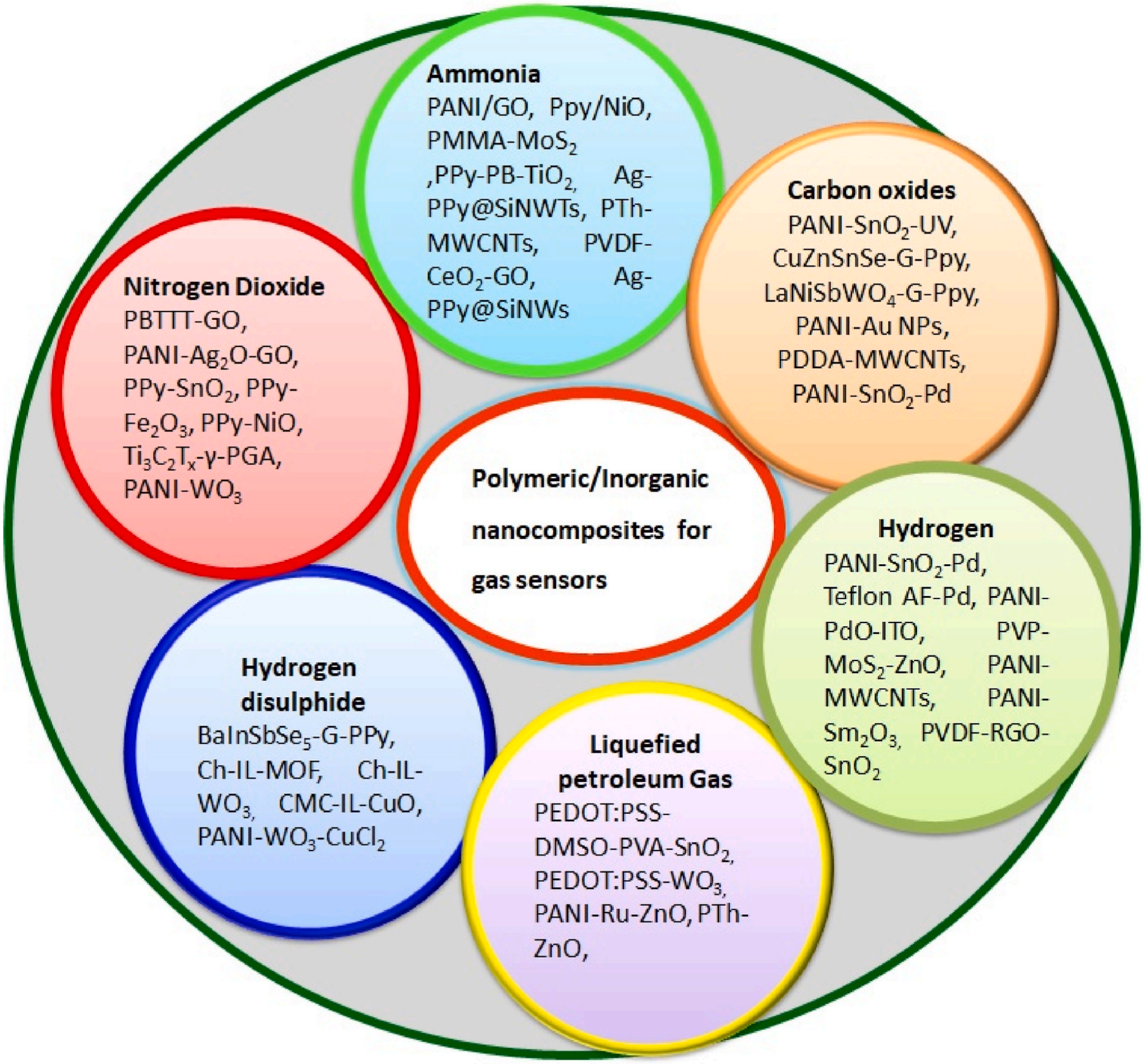

Fig. 3. Gas sensing applications of various polymeric/inorganic nanohybrids.

detection limit of prepared sensor was 100 ppb. The maximum response value for G-PANI-PVDF sensor was observed to fluctuate around 12% after 1500 bending/extension. This behaviour shows that the addition of graphene significantly enhances the bending stability of the prepared nanohybrid sensor. In addition to the sensitivity and stability, a good linear relationship between sensor response and temperature or relative humidity was also evident. The improved sensing behaviour of G-PANI-PVDF sensor was attributed to: (i) reversible acid-base doping process of PANI, (ii) effective charge transport route via graphene sheets, and (iii) multi-hierarchical porous structure provided by PVDF (Q. Wu et al., 2021).

Hu and his colleagues investigated the ammonia sensing ability of an intriguing material prepared by the polymerization of aniline on hollow nickel oxide (NiO) (Hu et al., 2021), as shown in Fig. 5. The hollow NiO–CuO structure was formed by solvothermal reaction followed by calcination. Then, CuO was etched in HCl and the polymerization of aniline was attained on the hollow structure, resulted in a spherical hollow composite of PANI-h-NiO. The sensor response was observed to be directly proportional to the concentration of ammonia, with a linear behaviour within the range of 1–10 ppm. The PANI-h-NiO sensor showed a better response of 43.1% at 10 ppm as compared to 28.7% and 12.6% for PANI-NiO and PANI, respectively. Furthermore, the composite sensor (PANI-h-NiO) displayed excellent selectivity for ammonia against water, VOCs and humidity along with the superb repeatability and long term stability. The excellent sensing performance of PANI-h-NiO sensor was related to two aspects: (i) larger surface area and more active sites provided by hollow structure, and (ii) p-p heterojunction at the interface between PANI and NiO (Hu et al., 2021).

Wang and co-workers reported the use of polyaniline (PANI) along with copper ferrite ($CuFe_2O_4$) to prepare the heterostructure composite, coated onto a substrate with electrodes, for high-performance ammonia sensing (Wang et al., 2020b). The experimental outcome revealed that the composite sensor (PANI-$CuFe_2O_4$) showed higher response of 27.37% at 5 ppm concentration of ammonia, which was significantly better than the one observed for pristine $CuFe_2O_4$ or PANI films. This superior sensing capability of as-synthesized composite sensor was associated to the p-n junction between PANI and $CuFe_2O_4$, which formed an electric field and converted the ammonia concentration into resistive changes. Therefore, this sensor presented an easier way to utilize PANI-$CuFe_2O_4$ nanohybrid sensor to detect lower concentrations of ammonia gas (Wang et al., 2020b).

Likewise, Fan and colleagues prepared the hierarchical nanohybrid sensor for ammonia detection using ultrasonic spray assisted in-situ polymerization to produce polyaniline (PANI) on tungsten trioxide (WO_3) nano-plates by intercalation-exfoliation process with varying molar ratios of aniline/WO_3 (Fan et al., 2020). The nanohybrid sensor

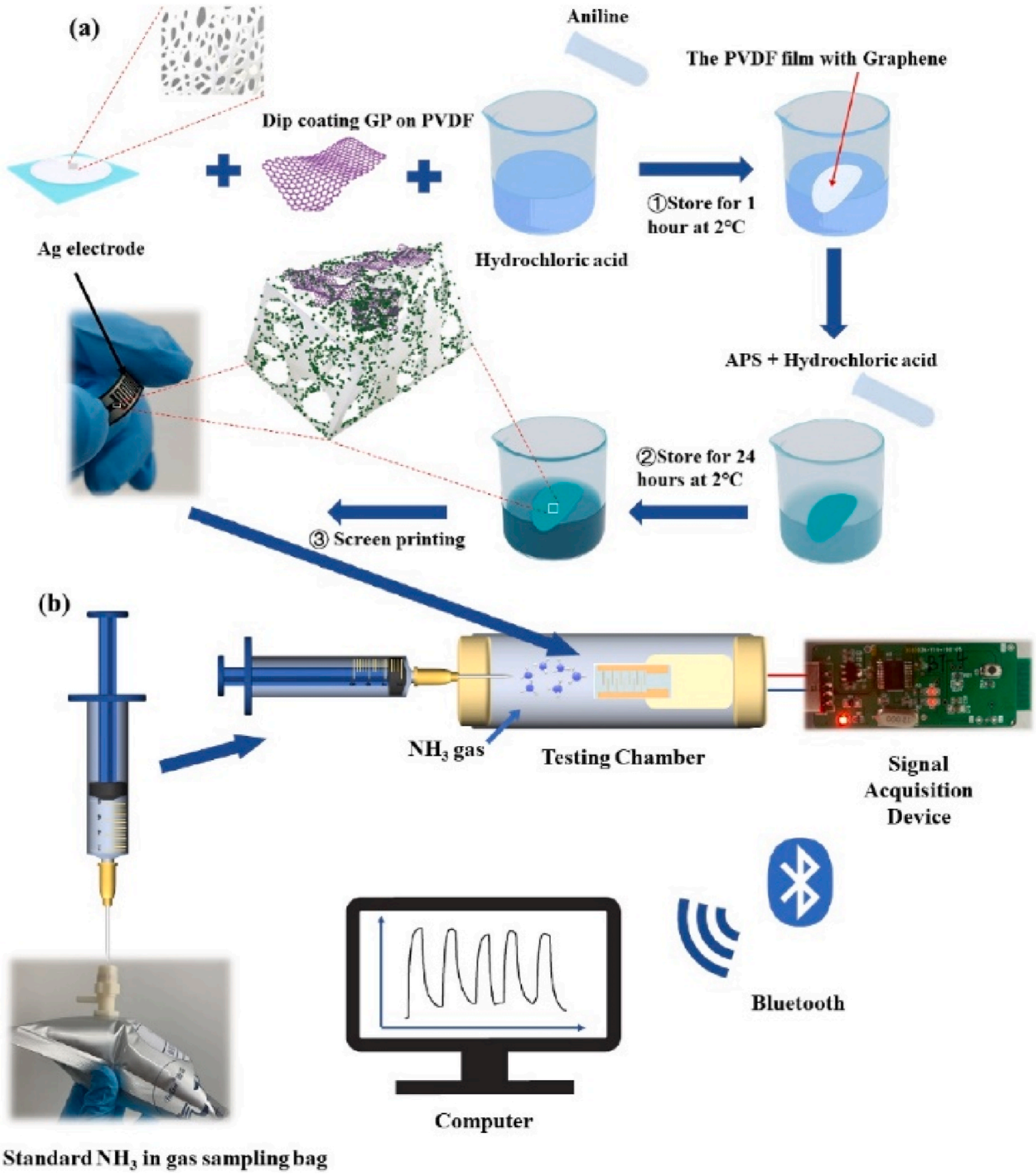

Fig. 4. (a) Fabrication scheme of G-PANI-PVDF sensor; (b) The schematics of testing system for gas sensing performance. Reprinted with permission from (Q. Wu et al., 2021).

(PANI-WO$_3$) displayed better ammonia sensing ability than the PANI nanocrystals or WO$_3$ nano-plates under same working conditions. At optimized molar ratio of aniline/WO$_3$ (2.5), the sensor exhibited a higher response of 34 at 100 ppm concentration of ammonia at room temperature. It was also observed that PANI primarily controlled the ammonia gas sensing properties of PANI-WO$_3$ sensor. A doping reaction (Fig. 6a) was found to occur as ammonia gas exposed to the sensor, which basically means the generation of NH$_4^+$ by capturing a proton from NH$^+$ group of PANI, which eventually resulted in the conversion of emeraldine salt (ES) to emeraldine base (EB), along with an increased resistance. In order to clearly understand the sensing mechanism, the possible energy diagram is presented in Fig. 6b and c. A typical p-n junction was formed at the interface between the p-type PANI and n-type WO$_3$, due to the difference in energy-gap of PANI and WO$_3$. In the presence of ammonia gas, a high resistance state was developed due to the capturing of holes from PANI by the NH$_3$ molecules and this lead to enhancement of depletion region of the p-n heterojunction. Moreover, the hierarchical structure of PANI-WO$_3$ nanohybrid provided the ample flow channels for ammonia gas, which eventually resulted in faster adsorption/desorption of NH$_3$ molecules, better electron transport and enhanced ammonia sensing process (Fan et al., 2020). Several other researchers have also reported the synthesis and ammonia sensing capability of nanohybrid sensor based on polyaniline and different nanomaterials including graphene oxide (Javadian-Saraf et al., 2021), MoS$_2$–SnO$_2$ (A. Liu et al., 2021), Nb$_2$CT$_x$ (Wang et al., 2021), SWCNTs (Ansari et al., 2020), MWCNTs (T. Wu et al., 2020a), CuO (Ahmadi Tabar et al., 2020), etc.

In addition to polyaniline (PANI), polypyrrole (PPy) has also been

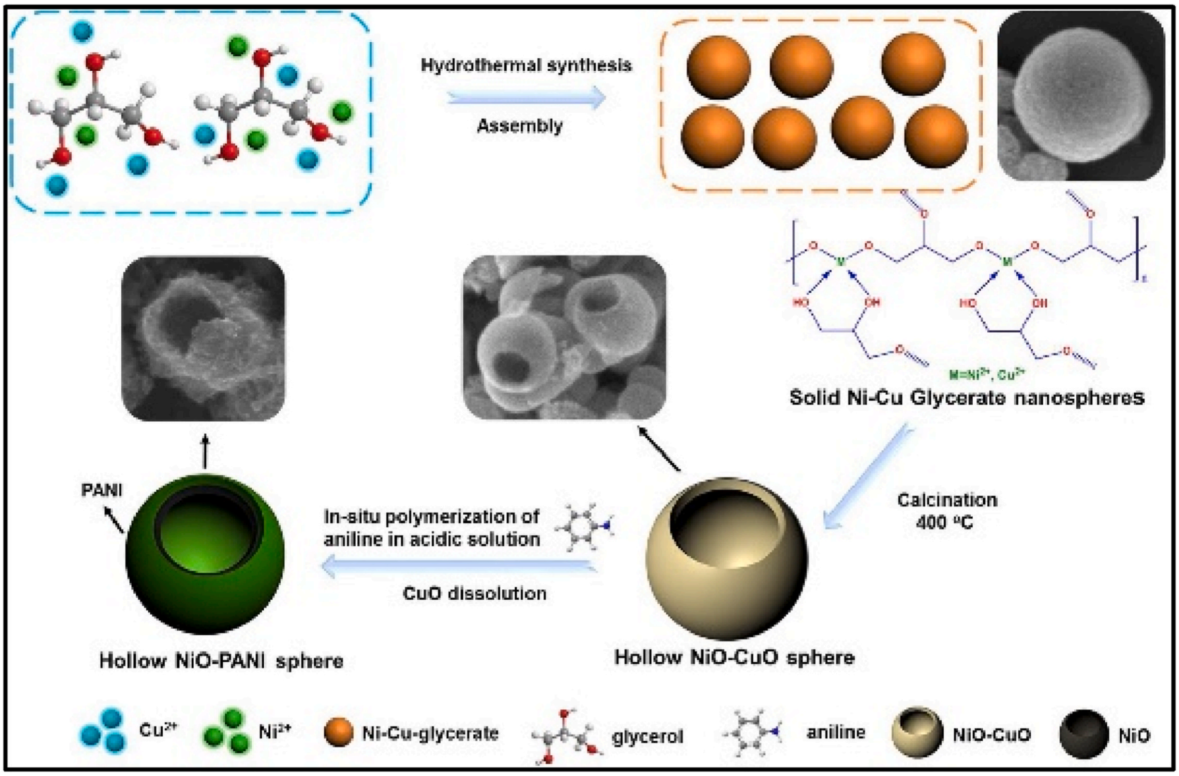

Fig. 5. Preparation scheme of PANI-h-NiO sphere composite for ammonia sensing at room temperature. Reprinted with permission from (Hu et al., 2021).

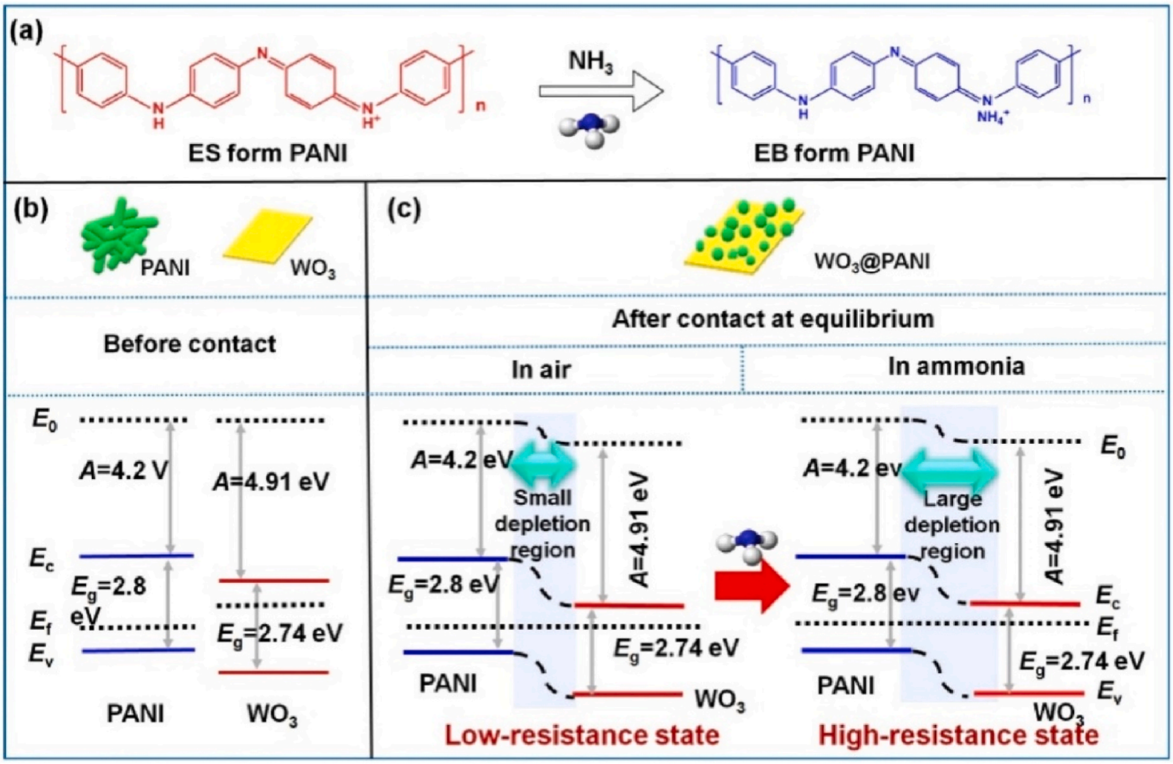

Fig. 6. (a) Reaction between PANI and NH_3 gas; Energy band diagrams of (b) PANI, WO_3 and (c) PANI-WO_3 heterojunction. Reprinted with permission from (Fan et al., 2020).

extensively used to fabricate the nanohybrid sensor for ammonia gas sensing. For instance, Qin and co-workers developed the composite sensor based on silver nanoparticles (Ag NPs) modified polypyrrole at silicon nanowires (SiNWs) for ammonia sensing under high humidity (Qin et al., 2020). The wrapping of PPy shell on loose silicon nanowires was achieved by vapour phase polymerization in the presence of $AgNO_3$

as an oxidant, which resulted in decorated Ag NPs on the PPy shell layer. The experimental results showed a higher response of 1.45–4.26 for 1–12 ppm concentration of ammonia at 80% relative humidity (RH), in case of Ag-PPy-SiNWs sensor. The response of Ag-PPy-SiNWs sensor (3.2) at 6 ppm was 78% and 208% higher than pristine PPy-SiNWs (1.8) and SiNWs (1.04), respectively (Qin et al., 2020). These results clearly indicated the efficacy of silver nanoparticles functionalization on the improvement of ammonia sensing ability of prepared sensor. Moreover, by increasing the humidity from 50% RH to 80% RH, the Ag-PPy-SiNWs sensor response decreased by 53%. The combined role of electronic sensitization, chemical sensitization and anti-humidity of the silver nanoparticles were mainly responsible for the enhanced ammonia sensing of Ag-PPy-SiNWs sensor, as compared to the sensors without the functionalization of Ag NPs. Therefore, this study presented a rapid, selective, ultrasensitive and reversible ammonia gas sensor under high humid conditions for clinical diagnosis. In addition to this, polypyrrole (PPy) has been utilized to prepare nanohybrid sensors for ammonia gas detection at room temperature by incorporating several nanomaterials such as TiO_2 (Muthusamy et al., 2021), SnO_2-GNR (Hsieh et al., 2021), NiO (Thi Hien et al., 2021), Ag–Ag_2O (Shoeb et al., 2021), graphene oxide (Shahmoradi et al., 2021), WO_3 (Albaris and Karuppasamy, 2020), V_2O_5-WO_3 (Amarnath et al., 2020), ZnO (P. Singh et al., 2021), Au (Li et al., 2020c), etc.

Abun and colleagues reported the fabrication of ammonia gas sensor through polymethyl-methacrylate (PMMA) supported exfoliation of molybdenum disulfide (MoS_2) multi-layered nano-sheets by ultrasonication technique (Abun et al., 2020). The results depicted an enhanced response of 54% for PMMA-MoS_2 sensor, which was tremendously superior to the bulk MoS_2 (15.2%) at 500 ppm concentration of NH_3. Furthermore, the as-synthesized PMMA-MoS_2 nanohybrid sensor showed outstanding selectivity to C_3H_6O, H_2 and CO_2. The higher sensing performance of PMMA-MoS_2 sensor was linked to the existence of structural defects and oxygen functional groups, which strongly enhances the sensing ability. Thus, the improved gas sensing characteristics of surface modified PMMA-MoS_2 nanohybrid sensors are quite favourable and sustainable as compared to the existing MoS_2 sensors for ammonia gas (Abun et al., 2020). Efficiency of various polymeric/inorganic nanohybrids for detection of ammonia has been given in Table 1.

3.2. Sensing of nitrogen dioxide

Among numerous greenhouse gases, nitrogen dioxide (NO_2) is recognized by World Health Organization (WHO) as one of the most dangerous, toxic and hazardous airborne contaminants (W. He, Zhao and Xiong, 2020). NO_2, a reddish-brown gas with pungent smell, is typically released into the atmosphere because of automotive exhaust, fossil fuels, thermal power plants, blasting of explosives, metal refining industries, ignition of propellants, food processing, etc. (Li et al., 2020a; Mirzaei et al., 2020; S. Zhao et al., 2019). This release of NO_2 causes a detrimental effect on environment such as acid rain, formation of ozone and photochemical smog (W. He et al., 2020; J. Wu et al., 2020b). Apart from this, the exposure of even lower concentrations of NO_2 can exert serious effects on human health including respiratory irritation, emphysema, asthma, bronchitis nausea, lung cancer, paralysis, and even death (Zhuang et al., 2019). NO_2 has also been identified as a biomarker for diagnosing gastric and lungs diseases (Z. Li, Liu, Guo, Guo and Su, 2018). Therefore, it is highly required to develop a selective, highly sensitive, reliable and stable gas sensor to detect NO_2 at room temperature for clinical diagnosis and environmental protection.

For example, Umar and colleagues examined the NO_2 sensing capability of nanohybrid sensor based on polyaniline-silver oxide-graphene oxide (PANI-Ag_2O-GO) (Umar et al., 2021). In order to fabricate the composite sensor, the dispersed solutions of graphene and PANI/Ag_2O in deionized water were mixed together (see Fig. 7a). The prepared mixture was then placed on the platinum microelectrodes fixed over the alumina ceramic chips (interdigitated electrodes) via drop and dry method (see Fig. 7b). The sensing performance of the composite sensor was estimated by a computerized characterization instrument (see Fig. 7c). The target gas was exposed to the sensor through the gas cylinder and the measurements were recorded by a data acquisition system. The results indicated the two-fold higher response for PANI-Ag_2O-GO sensor (5.85) as compared to the PANI (2.5) and PANI-Ag_2O (3.25) sensors, when exposed to 25 ppm NO_2 at 100 °C. The enhanced gas sensing response of nanohybrid sensor (PANI-Ag_2O-GO) was attributed to the charge transfers between the adsorbed NO_2 gas molecules and the nanohybrid surface. The adsorbed NO_2 molecules on the surface of PANI-Ag_2O-GO dissociated into nitric oxide (NO) or dinitrogen oxide (N_2O). This dissociation of NO_2 molecules was facilitated by π–π conjugation system formed between PANI and Ag_2O/GO, which eventually provided a huge π electronic cloud and excellent electron transfer path (see Fig. 7d). Thus, the presented sensor is an excellent candidate for detecting NO_2 gas at low temperature (Umar et al., 2021).

Similarly, polyaniline (PANI) was also used to fabricate a novel bilayer thin film sensor based on tungsten trioxide (WO_3) via hydrothermal process and in-situ chemical oxidative polymerization processes (W. He et al., 2020). This bilayer composite sensor was developed on the fluorine-doped tin oxide (FTO) glass substrate for NO_2 gas sensing. The experimental outcome showed three times higher response for composite sensor as compared to the pure WO_3 sensor, when the sensor was exposed to 30 ppm NO_2 at 50 °C. The lower detection limit of NO_2 for the fabricated composite sensor was 2 ppm. The improved gas sensing behaviour of composite sensor was attributed to (i) the formation of p-n junctions between n-type WO_3 and p-type PANI, (ii) the larger surface area, (iii) increased oxygen vacancies, and (iv) a broad conduction channel.

Recently, Zhao and colleagues exploited the blocking effect of γ-poly (l-glutamic acid) (γ-PGA) to enhance the NO_2 gas sensing performance of titanium carbide ($Ti_3C_2T_x$) (Q. Zhao et al., 2021). Titanium carbide nanosheets were prepared via a two-step procedure: (i) dispersion of titanium aluminium carbide (Ti_3AlC_2) in aqueous solution of hydrofluoric acid (etching solution) and (ii) incorporation of aqueous solution of tetramethylammonium hydroxide (TMAOH) for intercalation. The γ-PGA-$Ti_3C_2T_x$ composite was prepared by mixing aqueous solutions of $Ti_3C_2T_x$ nanosheets and γ-PGA. The composite sensor was then fabricated by spraying the γ-PGA-$Ti_3C_2T_x$ composite solution on the gold interdigitated electrode placed on the flexible polyimide substrate. The gas sensing characterization revealed the higher response of γ-PGA-$Ti_3C_2T_x$ composite sensor (1127.3%), which was observed to be 85 times than the response of $Ti_3C_2T_x$ sensor (13.2%). Furthermore, the as-synthesized γ-PGA-$Ti_3C_2T_x$ composite sensor not only displayed a shorter response and recovery times (43.4 s and 3 s), as compared to $Ti_3C_2T_x$ sensor (18.5 s and 18.3 s), but also exhibited a remarkable repeatability and reversibility at room temperature under 50% RH. This outstanding sensor response was associated to two aspects: (i) efficient adsorption of gas molecules and (ii) enhanced blocking effect from water molecules. The water film was observed to form on the surface of γ-PGA film by the adsorption of water molecules from the air on the surface. In the presence of lower concentration of NO_2, the reaction between gas molecules and water occurred and resulted in NO_3^- and H^+ ions, which ultimately reduced the film resistance. On the other hand, when the film was exposed to higher concentrations of NO_2, there was a competition between water molecules and gas molecules for the adsorption at the surface, which eventually created a blocking effect and an increase in film resistance. This competition was optimized by varying the $Ti_3C_2T_x$ amount in the composite, which further enhances the gas sensing capability. This study presented a unique way of enhancing the gas sensing properties of $Ti_3C_2T_x$ by γ-PGA modification (Q. Zhao et al., 2021).

Zhang and colleagues investigated the gas sensing properties of PPy-NiO nanohybrid sensor by varying the molar ratios of the individual components (Zhang et al., 2020b). At optimal molar ratio between PPy

Table 1
Literature survey on the sensing performance of polymeric/inorganic nanohybrids for ammonia gas.

Sensing materials	Target gas	Conc.	Response	Response time (s)	Recovery time (s)	Operating temp. (^oC)	Adv. Or disadv.	Ref.
PPy-PB-TiO_2	NH_3	100 ppm	78%	–	–	RT	High sensitivity and selectivity towards NH_3	Muthusamy et al. (2021)
PANI-GO	NH_3	–	–	150	400	RT	Low-cost and highly selective for NH_3	Javadian-Saraf et al. (2021)
PPy-SnO_2-GNR	NH_3	1 ppm	92.7%	–	–	RT	Outstanding repeatability and selectivity	Hsieh et al. (2021)
PEDOT:PSS-AVNF	NH_3	50 ppm & 100 p.m.	18.4% 260%	–	–	RT	Enhanced NH_3 sensitivity	Lee et al. (2021)
PANI-MoS_2-SnO_2	NH_3	100 ppm	1090%	21	130	RT	Good repeatability, acceptable flexibility and excellent selectivity	(A. Liu et al., 2021)
PANI-PVDF-G	NH_3	1 ppm	60%	46	198	RT	Excellent flexibility with stable response time after 1500 bending/extending cycles	(Q. Wu et al., 2021)
PANI-PET:NH_2-MWCNTs	NH_3	50 ppm	117%	47	–	RT	Good gas-sensing performance to NH_3	Ma et al. (2021)
PPy-NiO	NH_3	45 ppm & 350 ppm	65% 246.6%	12	178	RT	High sensitivity to NH_3 gas	Thi Hien et al. (2021)
PANI-Nb_2CT_x	NH_3	10 ppm & 50 ppm	74.68% 205.4%	218	300	RT	Superior selectivity, high sensitivity, low detection limit and good long-term reliability	Wang et al. (2021)
PANI-h-NiO	NH_3	10 ppm	43%	149	257	RT	Superb anti-interference along with the superior repeatability in 5 cycles and long-term stability in a week	Hu et al. (2021)
PPy-G-Ag-Ag_2O	NH_3	–	–	60	40	RT	Excellent selectivity toward NH_3	Shoeb et al. (2021)
PPy-SRGO	NH_3	–	–	48	234	28	Good repeatability and high selectivity to low-concentration ammonia	Shahmoradi et al. (2021)
PANI-RGO	NH_3	100 ppm	620%	219	541	RT	Remarkable long-term stability, good selectivity, low detection limit and low power consumption	Luo et al. (2021)
$LaNiMoSe_2$-G-PANI	NH_3	–	–	7–15	6–35	RT	Excellent detection ability with reproducibility	Oh et al. (2021a)
PANI-SnO_2	NH_3	7 ppm & 90 ppm	200%, 102%	44 33	915 33	RT RT	–	Feng et al. (2021)
PANI-SWCNTs	NH_3	10 ppm	24–25%	1–4	8–10	RT	Excellent stability up to four cycles for consecutive 10 days	Ansari et al. (2020)
PVP-CuO	NH_3	10 ppm	23.8%	17	15	RT	Highest sensitivity, excellent reproducibility, long-term stability and complete data reliability of 90 days with very small variation	Khan et al. (2020)
PPy-GO-WO_3	NH_3	10 ppm	58%	50	120	RT	Improved stability for the period of 50 days	Albaris & Karuppasamy (2020)
PPy-V_2O_5-WO_3	NH_3	50 ppm	85%	73	101	RT	High selectivity towards NH_3 gas	Amarnath et al. (2020)
PANI-PVDF-MWCNTs	NH_3	1 ppm	32%	76	26	RT	Good flexibility and minor decline in response value after 500 bending cycles	(T. Wu et al., 2020b)
PANI-$SrGe_4O_9$	NH_3	10 ppm	208%	62	223	RT	Supersensitive and ultra-low detection limit	(Y. Zhang et al., 2020a)
PANI-$CuFe_2O_4$	NH_3	5 ppm	27.37%	84	54	RT	Excellent sensitivity toward NH_3 gas	Wang et al. (2020b)
PMMA-MoS_2	NH_3	500 ppm	54%	10	14	RT	Excellent sensitivity and selectivity	Abun et al. (2020)
Ag-PPy@SiNWs	NH_3	6 ppm	320%	<6	94	RT	Excellent NH_3 sensing	Qin et al. (2020)
PTh-MWCNTs	NH_3	2000 ppm	88.7%	100	90	RT	Extraordinary sensitivity, reversibility, selectivity and stability	Husain et al. (2020)
PANI-Ph-RGO	NH_3	100 ppm	773%	300	800	RT	Low detection limit, good stability and selectivity, wireless, chip less, and potentially fully printable	Tanguy et al. (2020)
PPy-GO-$LiCuMo_2O_{11}$	NH_3	–	–	50	45	RT	Higher sensing performance and selectivity	Oh et al. (2020)
PANI-CuO@3D-NGF	NH_3	100 ppm	930%	30	57	RT	Outstanding low detection limit, excellent sensing performance and cheaper	Ahmadi Tabar et al. (2020)
P3HT-RGO-MWCNTs	NH_3	10 ppm	3.6%	30	–	RT	–	Khanh et al. (2021)
PVDF-CeO_2-GO	NH_3	50 ppm	1232%	106	11	RT	Strong response to NH_3 gas with enhanced gas sensing properties	Deshmukh & Pasha (2020)
ZnO-en-PPy	NH_3	–	–	45	55	RT	Stability for 90 days	(P. Singh et al., 2021)
PPy-Au	NH_3	100 ppm	2650%	7	7	RT	Stable and ultrahigh sensitivity even during repeated deformation	Li et al. (2020c)
PANI-WO_3	NH_3	100 ppm	3400%	~30	~390	RT	Excellent stability and selectivity	Fan et al. (2020)
PANI-GO-ZnO	NH_3	300 ppm	–	2	164	–	Fast response	Gaikwad et al. (2017)
PANI-WO_3	NH_3	100 ppm	121%	32	–	RT	Strong response to ammonia	Kulkarni et al. (2019)

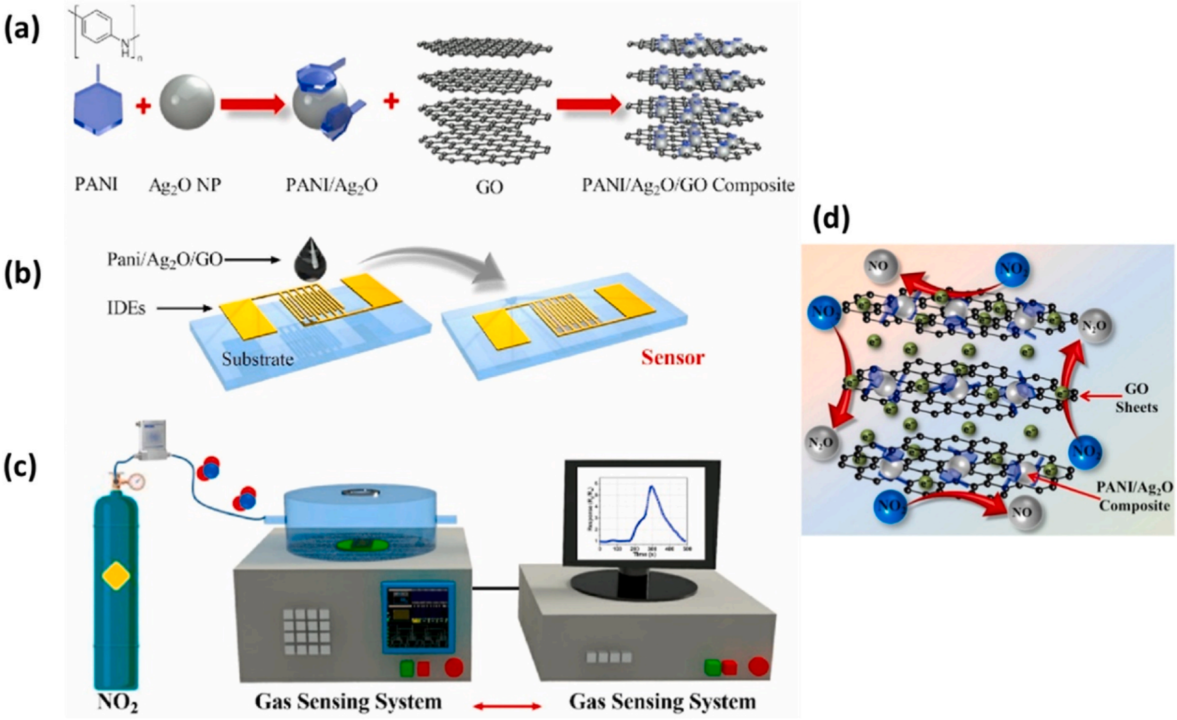

Fig. 7. Pictorial representation for synthesis of (a) PANI/Ag_2O nanoparticles and PANI-Ag_2O-GO composite; (b) Production of gas sensor; (c) Measurement of NO_2 sensing performance on prepared sensor; (d) Gas sensing mechanism of prepared PANI-Ag_2O-GO nanohybrid sensor for NO_2 gas. Reprinted with permission from (Umar et al., 2021).

and NiO, the response of the composite sensor (PPy-NiO) was 30 times higher than the bare NiO sensor along with the lower detection limit of 49 ppb. The flow of electrons from PPy to NiO resulted in greater variation in hole concentration and enhanced carrier mobility before or after NO_2 exposure (J. Zhang et al., 2020a). This heterojunction resistance was reduced by further increasing the molar concentration of PPy, which eventually resulted in lower sensitivity of prepared nanohybrid sensors. Thus, a suitable amount of PPy is important to fabricate a sensitive composite sensor for NO_2 detection. In addition to NiO, several other nanomaterials such as SnO_2 (Sakhare et al., 2021), graphene oxide (Guettiche et al., 2021), Fe_2O_3 (Wang et al., 2020a), etc. were also reported to fabricate PPy based nanohybrid sensors for detecting NO_2 gas. The sensing performance of different polymeric nanohybrid for NO_2 gas has been provided in Table 2.

3.3. Sensing of hydrogen

Hydrogen (H_2) gas is colourless, odourless, tasteless and highly flammable under normal conditions when released into the air (Ibraheem et al., 2021). It is widely used in many industries such as metal smelting, semiconductor processing, petroleum extraction, chemical processing and glassmaking because of its strong reducing

Table 2
Literature survey on the sensing performance of polymeric/inorganic nanohybrids for NO_2 gas.

Sensing materials	Target gas	Conc.	Response	Response time (s)	Recovery time (s)	Operating temp. (°C)	Adv. Or disadv.	Ref.
PANI-Ag_2O-GO	NO_2	25 ppm	585%	100	140	100	Stability for 6 days	Umar et al. (2021)
GO-PEDOT: PSS-LGS	NO_2	100 ppm	570%	35	10	RT	Good cycling stability, excellent sensitivity and a low detection limit	Pasupuleti et al. (2021)
PPy-RGO: aryl:COOH	NO_2	2 ppm	30%	129	114	RT	Good functionality and stability under harsh environment	Guettiche et al. (2021)
PBTTT-GO	NO_2	10 ppm	174%	75	523	RT	Simple fabrication process for mass production and low cost	Sahu et al. (2020)
PPy-SnO_2	NO_2	100 ppm	53.7%	33	881	RT	Highest selectivity towards NO_2 gas together with reproducibility kinetics	Sakhare et al. (2021)
$Ti_3C_2T_x$-γ-PGA	NO_2	50 ppm	1127.3%	43	3	RT	High response kinetics, good repeatability, reversibility, and baseline stability. The batch consistency needs to be improved for practical applications along with the service life.	(Q. Zhao et al., 2021)
PPy-Fe_2O_3	NO_2	10 ppm	221%	150	879	50	High selectivity and response to NO_2	Wang et al. (2020a)
PPy-NiO	NO_2	60 ppm	4500%	–	–	RT	–	(J. Zhang et al., 2020a)
PANI-WO_3	NO_2	2 ppm	118%	–	–	50	Good stability and selectivity	(W. He et al., 2020)
PPy-*p*TSA-Ag	NO_2	100 ppm	68%	148	500	RT	Fast response and great reproducibility	Karmakar et al. (2017)

characteristics. Moreover, hydrogen can be utilized for environmental, biomedical and seismic monitoring for detecting particular type of environmental pollution, bacterial diseases, etc. (Punetha et al., 2020). Due to its high energy content, low molecular weight and combustibility without producing any toxic gases (De Vrieze et al., 2020; Pareek et al., 2020), it is considered as a valuable source of carbon-free energy for many industries including fuel cell, nuclear, space and automobile (Frischauf, 2016). However, its applications are seriously restricted by its explosive nature for wide range of concentrations (4–75 vol%) (Punetha et al., 2020). Therefore, the development of sensors to detect even minute concentrations of H_2 is critically required.

For instance, Ostergren and colleagues reported the fabrication of nanohybrid sensor based on fluorinated polymer (Teflon AF) and colloidal palladium (Pd) nanoparticles for efficient plasmonic sensing of H_2 (Östergren et al., 2021). The continuous flow process was used to prepare the single crystal Pd nanoparticles coated with polyvinylpyrrolidone (PVP) (see Fig. 8a). The TEM images showed the uniform cubic shape and a narrow particle size distribution (PSD) of the prepared Pd nanoparticles (see Fig. 8b). The nanohybrid was synthesized by mixing the polymer powder with the nanoparticle suspension. In the end, the mixture was processed in a micro-extruder to form filaments of nanohybrid, which were then either melt-pressed to form plate or 3D printed to form complex shape. The complete dispersion of Pd nanoparticles, without any aggregation, into the polymer matrix was verified by the TEM images of cryo-fractured composite plates (see Fig. 8c). However, the nanoparticles were transformed into spherical shape from the cubic shape having sharp edges, which was linked to the processing at high temperatures (250 °C). The colour of the melt-pressed plates was observed to be completely transparent for Teflon AF while dark brown for composite plate having 6.2×10^{-3} vol% Pd (see Fig. 8d), which was associated to the localized surface plasmon resonance (LSPR) of the nanoparticles. The gas sensing results showed a faster response time of 2.5 s for 100 μm thick nanohybrid (Teflon AF-Pd) plate exposed to H_2 gas, along with the lower detection limit of 30 ppm. Furthermore, the nanohybrid material was 3D printed to form a sensor cap, which can be fitted on a standard optical fibre connector. The outcome displayed that the sensor cap was quite robust in sensing H_2 for multiple exposures (100 times) at 40,000 ppm. This research demonstrated a viable route for melt-processing the polymer-Pd nanohybrids for plasmonic sensing of H_2 (Östergren et al., 2021).

As already described for other gases, polyaniline (PANI) has been used to fabricate composite sensors for remarkable sensing of H_2 gas as well. For example, Pippara and colleague fabricated a unique composite film based on the amalgam of polymer, metal and semiconductor for H_2

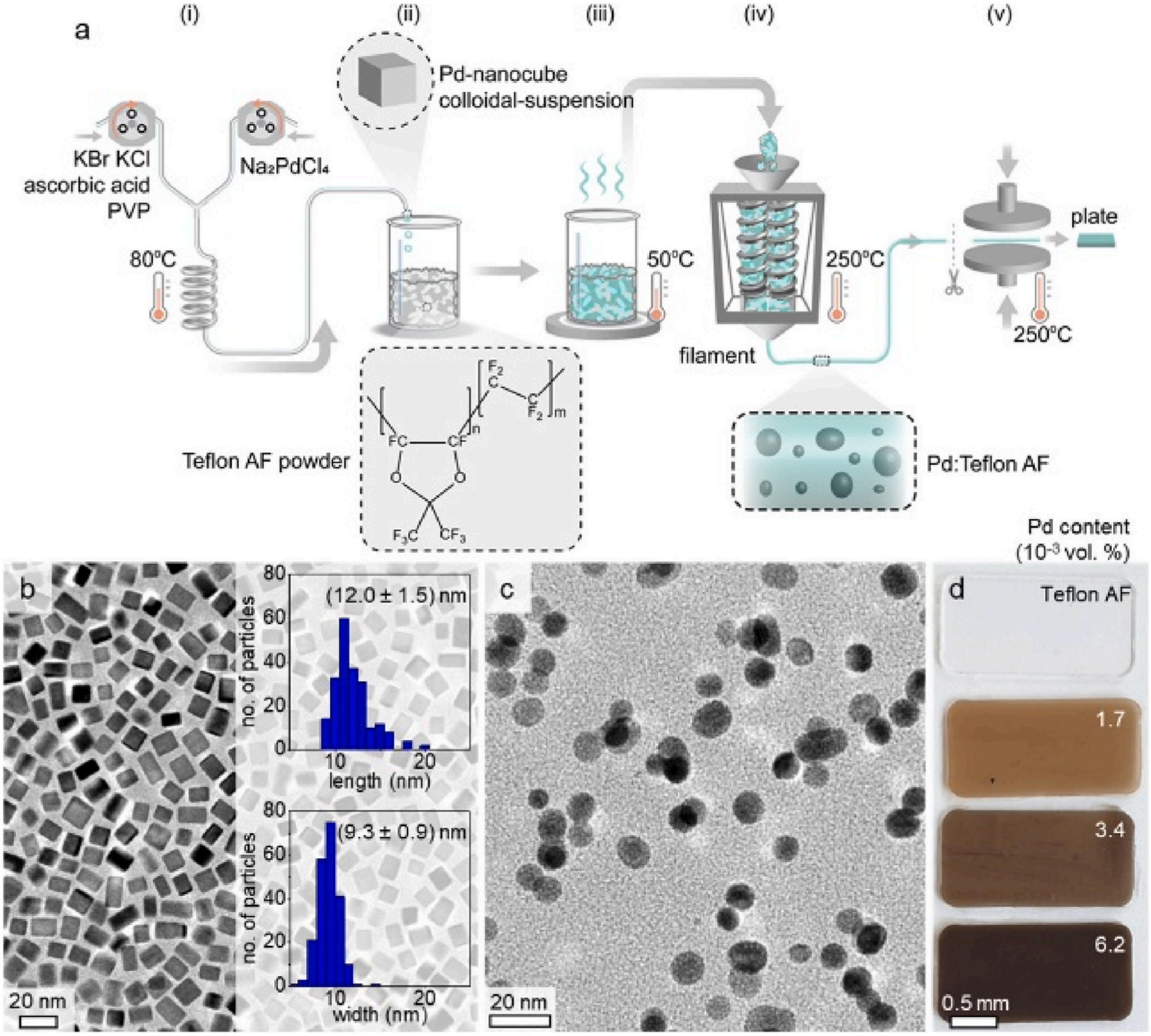

Fig. 8. (a) Preparation of nanohybrid material involving (i) synthesis of PVP-coated Pd nanoparticles, (ii) mixing of Pd nanoparticle suspension with the polymer, (iii) drying of Pd-polymer mixture, (iv) melt extrusion, and (v) melt pressing; (b) TEM image of Pd nanoparticles with length and width histograms; (c) TEM image of Pd nanoparticles incorporated in Teflon AF and (d) melt-pressed plates of neat Teflon AF and its nanohybrids (0.5 mm-thick) Reprinted with permission from (Östergren et al., 2021).

gas sensing at room temperature (Pippara et al., 2021). Nanohybrid film, based on tin oxide (SnO_2) nanosheets and PANI doped with Pd, was prepared via hydrothermal process. The computational results showed a considerable improvement in the H_2 sensitivity of (i) SnO_2 because of doping with Pd and (ii) PANI due to the presence of SnO_2. The gas sensing experiments revealed a highest sensitivity of 540% for the SnO_2–Pd film at 4000 ppm of H_2 while the highest performance factor was observed for the composite film, PANI-SnO_2-Pd (Pippara et al., 2021). Likewise, Arora and Puri developed a hetero-structure composite sensor based on polyaniline (PANI), palladium oxide (PdO) and indium tin oxide (ITO) for H_2 gas sensing at room temperature (Arora and Puri, 2020). Nanohybrid (PANI-PdO) was prepared by using in-situ wet chemical polymerization process. The prepared nanohybrid was then deposited on the ITO layer coated glass substrate via spin coating technique. The gas sensing results displayed a two fold increase in the sensitivity of the composite sensor (PANI-PdO-ITO) at 10,000 ppm of H_2, as compared to the bare PANI sensor. Moreover, this sensitivity of composite sensor also showed an increase with the increasing content of PdO from 5 wt% to 10 wt% (Arora and Puri, 2020). Hence, the authors presented a facile and economical approach for fabricating highly efficient, responsive, sensitive and handheld H_2 gas sensors, without the requirement of expensive interdigitated electrodes. Same polymer (i.e., PANI) was also used to develop composite sensors for H_2 gas based on other nanomaterials such as Sm_2O_3 (Jamnani et al., 2020), MWCNTs (Bafandeh et al., 2020), etc.

Goel and colleagues presented a hybrid sensor (PVP–MoS_2–ZnO) for H_2 gas detection at lower temperatures (Goel et al., 2021). The hybrid film was prepared by decorating the surface of ZnO film (obtained via magnetron sputtering) with the variable concentrations of MoS_2-PVP nanohybrid (prepared through polymer supported liquid exfoliation). This decoration was found to increase the surface area and the number of adsorption sites for H_2 molecules, which eventually enhanced the gas sensitivity. At optimal concentration of MoS_2-PVP (i.e., 5 mg/mL), the composite sensor (PVP–MoS_2–ZnO) exhibited almost 8 times higher sensing response than the bare ZnO sensor at 50 ppm H_2 concentration. The enhanced sensing capability of as-fabricated composite sensor (PVP–MoS_2–ZnO) was attributed to the (i) spill-over effects and (ii) electronic sensitization (ES). Hence, the reported hybrid sensor with excellent hydrogen sensing ability indicated a significant role of PVP-MoS_2 in hydrogen detection (Goel et al., 2021).

Similarly, Punetha and colleagues developed a tertiary nanohybrid sensor based on polyvinylidene fluoride (PVDF) polymer and two nanomaterials including tin oxide (SnO_2) and reduced graphen oxide (RGO) for H_2 gas sensing (Punetha et al., 2020). The hot press method was used to fabricate the nanohybrid film having fixed concentration ratio between polymer and nanomaterials (0.9 and 0.1), however, with varying ratios between both nanomaterials (SnO_2 and RGO). The sensor was fabricated by placing the composite film on the interdigitated chromium electrode via electronic beam evaporation technique. The experimental outcome showed that the composite sensor (PVDF-SnO_2-RGO) having 0.75/0.25 ratio between SnO_2/RGO exhibited 49.2% sensing response and 34 s response time at 100 ppm concentration of H_2 (Punetha et al., 2020). This tertiary nanohybrid sensor explored a new way to fabricate reliable, flexible and high performance sensor for H_2 gas (Table 3).

3.4. Sensing of hydrogen sulfide

Hydrogen sulfide (H_2S) is a colourless, toxic, extremely hazardous, highly corrosive, combustible, and potentially lethal gas primarily recognized from its smell of rotten eggs (Cheng et al., 2019). It is extensively produced in large quantities from various industries including wastewater treatment, petroleum refining, coke ovens, leather manufacturing, paper mills, food processing, mining industry, livestock farming, glue manufacturing and construction (A. Ali et al., 2021; Xu and Townsend, 2014). H_2S is also emitted from the natural sources such as natural gas, crude petroleum, volcanos, hot spring and the bacterial breakdown of human, animal and food wastes in the absence of oxygen (F. I. M. Ali et al., 2020a; R. He, Xia, Bai, Wang and Shen, 2012). The exposure of this lethal gas at lower concentrations can cause severe health effects including sore throat, dizziness, eye inflammation, headache, damaging respiratory and nerve system, poor memory and losing consciousness (Y. Wang et al., 2020c). However, at very high concentrations of H_2S, immediate death can also occur which makes it a silent killer (Kimura, 2011). Therefore, an efficient and faster detection of H_2S gas are crucial for protecting human health and environment.

Metal organic frameworks (MOFs) possess highly ordered structure, ultra-porosity and great surface area for adsorption (Mehtab et al., 2019; Rasheed et al., 2020; Rasheed and Rizwan, 2022). The geometry of metal and structure of linkers give an ordered framework with strong bonds which is an important requirement for the stability of sensor material. MOFs possess tuneable pores, great catalytic potential and thermal stability. Owing to these features, MOFs are widely used in sensing of volatile organic compounds. MOFs possess great synthetic-flexibility which made them eligible for tuning of mechanical, electrical and optical features. MOFs have high energy band gap due to the use of insulating ligands and also bad overlapping between p orbitals of the ligands and d-orbitals of metal ions. Due to these issues, MOFs do

Table 3
Literature survey on the sensing performance of polymeric/inorganic nanohybrids for hydrogen gas.

Sensing materials	Target gas	Conc.	Response	Response time (s)	Recovery time (s)	Operating temp. (^oC)	Adv. Or disadv.	Ref.
PANI-SnO_2-Pd	H_2	50 ppm & 350 ppm	19.2%, 353.7%	39	53	RT	–	Pippara et al. (2021)
Teflon AF-Pd	H_2		–	2.5	–	RT	Robust sensing in a long term test of 100 exposures	Östergren et al. (2021)
PVP-MoS_2-ZnO	H_2	50 ppm	46%	–	–	150	Superior hydrogen sensing	Goel et al. (2021)
PANI-PdO-ITO	H_2	10000 ppm	175%	3	4	RT	Highly sensitive towards H_2 gas	Arora & Puri (2020)
PANI-Sm_2O_3	H_2	10000 ppm	394%	3	7	RT	Excellent repeatability	Jamnani et al. (2020)
PANI-MWCNTs	H_2	4000 ppm	24%	48	55	0	Good repeatability, sustainability and selectivity	Bafandeh et al. (2020)
PVDF-RGO-SnO_2	H_2	100 ppm	49.2%	34	142	RT	Low-cost, flexible and wearable sensor	Punetha et al. (2020)
PANI-SnO_2	H_2	6000 ppm	42%	11	7	30	Fast response and great sensitivity	Sonwane et al. (2019)
PPy-Pd-TiO_2	H_2	10000 ppm	8.1%	220	100	25	Great stability and selectivity	Zou et al. (2016)
Ni–Pd-SWCNTs	H_2	–	10%	720	60	25	–	(García-Aguilar et al., 2014)
MWCNTs-TiO_2-Pt	H_2	500 ppm	3.9%	–	–	RT	–	Dhall et al. (2017)

not show electrical conductivity which is a major requirement for sensors development (Ghanbarian et al., 2018). Polymeric materials possess novel electrical features and they are easy to synthesize. Alternating single and double bonds are present in polymer chains, therefore, delocalization of pi electrons occur along the chain and this charge delocalization provides many active sites for desorption and adsorption of target gas molecules. Thereof, integration of MOFs with polymeric materials can incorporate charge conduction feature in them and generation of hollow metal oxides based MOFs may possess excellent potential in sensing applications (C.-S. Liu, Li and Pang, 2020). A novel composite sensor based on polymer mixed-matrix membrane and metal organic framework (MOF) for efficient sensing of H_2S gas at room temperature has been developed (A. Ali et al., 2021). The composite film was prepared by mixing the chitosan solution, ionic liquid (glycerol) and MOF. The sensor was fabricated by mounting the composite film between copper and stainless steel plates. The experimental results showed an increase in the measured current signal as a function of increasing gas concentration. After stopping the gas flow and flusing the chamber with N_2 gas, the response reduced to its original values within 30 s, which represented the reversibility of the sensor (see Fig. 9a). The enhanced sensing of composite sensor was attributed to the presence of amino and hydroxyl groups in chitosan and ionic liquid, which eventually provided the unbonded electrons and facilitated the proton conductivity throughout the membrane (see Fig. 9b). On the other hand, MOF provided extra sites for interaction with the H_2S molecules by having multiple oxygen atoms with unbounded electrons. The composite sensor was observed to efficiently detect the H_2S gas up to 1 ppm, which was 15 times higher than the sensing response of polymer membrane without MOF. This behaviour revealed that the incorporation of MOF nanoparticles boosted the proton conductivity of polymer membrane by providing extra interactions sites, open porous and hierarchical structure. However, this sensing response can further be enhanced by playing with the pore structure, pore size, pore shape, type of MOF, etc. which needs further systematic investigation. Therefore, the as-fabricated polymer-MOF composite sensor is a suitable candidate for H_2S detection at room temperature because of its excellent selectivity, response time, reproducibility and stability. In addition to MOF, same research group has also investigated the H_2S gas sensing ability of chitosan/ionic liquid flexible membrane by incorporating either CuO (F. I. M. Ali et al., 2020b) or WO_3 (F. I. M. Ali et al., 2020a; T Shujah et al., 2019a,b) nanoparticles.

Likewise, in addition to chitosan, Hittini et al. investiagted the H_2S gas sensing behaviour of carboxymethyl cellulose (CMC) and ionic liquid (glycerol) based flexible membrane modified with copper oxide (CuO) nanoparticles (Hittini et al., 2020). The nanoparticles of required size were synthesized by using microwave supported hydrothermal method. The polymeric solution (CMC-IL) was mixed with different amounts of nanoparticles and the resultant membrane was placed between two electrodes to fabricate the H_2S gas sensor. The sensor showed faster response and higher sensitivity at low concentration of H_2S gas (15 ppm) and at low temepratures. Furthermore, the sensor was highly selective towards the target gas along with the low humidity dependence. The sensor response was observed to increase by increasing the nanoparticles concentration from 2.5 to 5% while the sensor response remained the same by futher increase up to 7.5%. This behaviour was attributed to the increase in reactive sites till 5% of nanoparticles and to the aggolmeration of nanoparticles by further increase in their concentration. Therefore, this study presented an interesting organic-inorganic hybrid sensor for H_2S gas sensing in harsh environments with low power consumption and good sensitivity (Hittini et al., 2020).

Belkhamssa et al. reported the fabrication of polyaniline-copper chloride (PANI-$CuCl_2$) and polyaniline-tungsten trioxide-copper chloride (PANI-WO_3-$CuCl_2$) composite sensors for H_2S detection (Belkhamssa et al., 2021). The sensor was prepared by drop casting the composite solution on the carbon electrodes, which were screen printed on polyethylene terephthalate (PET) substrate. The experimental outcome revealed a reduction in the response time from 15 min to 4 min and insensitivity to humidity till 40% by incorporating WO_3 nanoparticles within the PANI-$CuCl_2$ composite. The results further showed the working range of the composite sensor from 0.1 to 1 ppm along with the limit of detection of 155 ppb. The enhanced sensing properties of tertiary composite (PANI-WO_3-$CuCl_2$) sensor was attributed to the (i) formation of p-n heterojunction between n-type WO_3 and p-type PANI and the enhancement in the oxygen adsorption capacity of PANI-WO_3 composite, (ii) formation of copper sulfide due to the reaction between H_2S and $CuCl_2$, which eventually increased the carrier concentration and decreased the resistance of sensor. Moreover, this resistance change of sensor was also linked to the partial sulfidation of WO_3 in the presence of H_2S. Hence, the excellent selectivity, fast response and good repeatability of the composite sensors made them quite useful for H_2S detection in industrial applications (Belkhamssa et al., 2021).

Oh and colleagues studied the H_2S gas sensing properties of novel nanohybrid sensors based on quaternary semiconductor ($BaInSbSe_5$), graphene and polypyrrole (Oh et al., 2021c). In contrary to the traditional sensors based on polypyrrole, this study simplifies the operation of sensors for real sample analysis due to the presence of semiconductor. The sensor exhibited very fast response time (<1 s) and recovery time (<1 s) at room temperature for 300 ppm of H_2S gas. The excellent sensing performance of the sensors was associated to the high adsorption capacity and low band energy gap. Therefore, the fabricated sensor is a potential candidate for environmental and industrial applications due to its highly stable sensitivity and selectivity along with the outstanding repeatability (Oh et al., 2021c). Sensing performance of different polymeric/inorganic nanohybrids for detection of hydrogen sulphide has

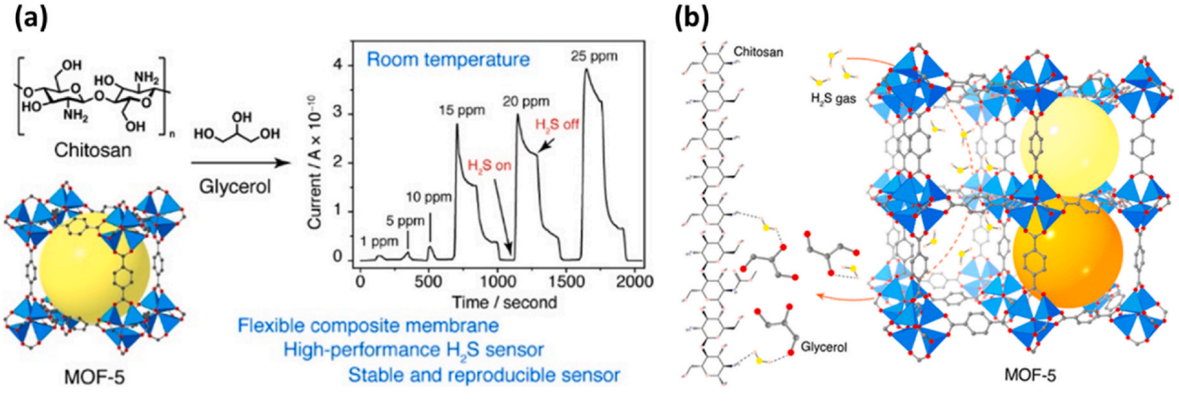

Fig. 9. (a) Electrical current signal of Ch-IL-MOF composite sensor as a function of H_2S concentration and time; (b) Pictorial representation of proposed H_2S gas-sensing mechanism. Atom colors: S, yellow; Zn, aqua; O, red; N, blue; C, grey; and H, pastel red. Reprinted with permission from (A. Ali et al., 2021). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

been given in Table 4.

3.5. Sensing of carbon oxides (CO_2 and CO)

Nowadays, most of the countries have taken different steps to limit global warming (i.e., temperature variations, oceanic fermentation, etc.) which are critically important to avoid catastrophic levels of greenhouse gases. Although CO_2 is an important part of the photosynthesis process, it is one of the odourless and colourless greenhouse gases which enter into the atmosphere through fossil fuels, burning trees, factories reactions, etc. (Jeong et al., 2016). The human exposure to CO_2 above certain concentrations (>5000 ppm) can cause serious health issues such as respiratory disorders (Ha et al., 2018). On the other hand, CO_2 is extensively used for producing carbonated drinks and pneumatic frameworks. Moreover, the detection of CO_2 gas in human breath can provide non-invasive and early diagnosis of gastric malignancies (Van Marcke, Daoudia, Penaloza and Verschuren, 2015). CO is another odourless, colourless and a toxic gas which is primarily produced by the incomplete combustion of fuels (natural gas, gasoline, coal, wood, etc.) in gas fires, car engines and domestic appliances (Mahendraprabhu et al., 2019). The human exposure to lower concentrations of CO can create nausea, dizziness, headache, vomiting and unconsciousness (Hsu et al., 2020). Conversely, the moderate to higher concentrations of CO (800–6000 ppm) can significantly affect the amount of oxygen carried by haemoglobin in the human body and can ultimately cause the heart diseases (Roy et al., 2020; Tahira Shujah et al., 2019). Thus, the development of smart and reliable sensors for detecting minute levels of CO_2 or CO is urgently needed to control and monitor its concentrations for various applications.

Riyazi and azim examined the carbon dioxide (CO_2) gas sensing performance of capacitive-type nanohybrid sensor based on polypyrrole (PPy) and copper phthalocyanine (CuPc) (Riyazi and Azim Araghi, 2020). First of all, PPy was prepared from its monomer via one-step reaction of chemical oxidative polymerization by using ammonium persulfate (APS) in an acidic media (HCl). The nanohybrid (PPy-CuPc) were then fabricated by in-situ chemical oxidative polymerization method with or without the addition of cationic surfactant, cetyltrimethylammonium bromide (CTAB) within the temperature range of 0–5 °C. The SEM images revealed the formation of interconnected network of nanofibers by incorporating CTAB in PPy-CuPc mixture, which eventually resulted in higher response and sensitivity as compared to the PPy-CuPc nanohybrids without CTAB and pure PPy, due to their particulate morphology. This enhanced sensing performance of PPy-CuPc nanohybrids in the presence of CTAB was associated to the (i) porous structure of sensing layer which facilitated the diffusion of gas molecules, (ii) high surface-to-volume ratio of nano-fibrous structure of PPy, (iii) interconnected network of PPy nanofibers, and (iv) synergistic effect of properties of individual components (PPy and CuPc). Hence, this interesting approach can be utilized to produce reliable, innovative, cheaper and sensitive nanohybrid sensors based on phthalocyanine and other conducting polymers for different commercial applications (Riyazi and Azim Araghi, 2020).

Kumar and colleagues reported the fabrication of PPy-MWCNTs nanohybrids using chemical oxidative polymerization technique for CO_2 gas sensing at room temperature (Kumar et al., 2020). The morphological analysis confirmed the nano-crystalline structure of PPy-MWCNTs with a minimum crystallite size of 8.1 nm. The nanotubes were found to be completely wrapped by the polymer, which enhanced the sensitivity of the sensor. The as-fabricated sensor displayed highest sensing response (7.2) for 1000 ppm of CO_2 and maximum sensitivity of 41.33 kΩ/%RH for humidity at room temperature. Moreover, the prepared sensor also exhibited excellent selectivity towards CO_2 among acetone, LPG and ethanol. The sensing mechanism of prepared nanohybrid sensor was linked to the increase in resistance upon exposure of CO_2 (see Fig. 10). The chemisorbed oxygen captured a free electron from the conduction band, which decreased the concentration of electrons inside the film and increased the depletion layer, which means increase in resistance (Kumar et al., 2020).

Roy and colleagues designed a resistive-type nanohybrid sensor based on poly (diallyldi-methylammonium chloride) (PDDA) and MWCNTs for efficient and low-level sensing of carbon monoxide (CO) at room temperature (Roy et al., 2020). The results of gas sensing experiments showed the sensitivity value of 11.51 for 20 ppm of CO. The prepared sensor was suitable to detect very low concentrations of CO ranging from 1 to 20 ppm along with the detection limit of 127 ppb. Moreover, the sensor response was observed to increase by increasing the temperature up to 100 °C. The sensing mechanism of the sensor was explained by the charge transfer from CO molecule to positively charged quaternary ammonium group available on PDDA, which eventually resulted in higher current from the sensor. On the removal of CO molecule, the ammonium group regained its electrons, which ultimately reduced the current. The sensor can be fabricated on any flexible substrate to have portable CO sensor for monitoring indoor air quality and also for industrial applications (Roy et al., 2020).

Nasrefahani and colleagues demonstrated the CO gas sensing performance of nanohybrid sensor based on PANI and gold (Au) nanoparticles (NPs) prepared via ultrasonic mixing of PANI with different amounts of Au NPs (Nasresfahani et al., 2020). The SEM micrographs showed the deposition of negatively charged Au NPs onto the positively charged PANI fibres due to the hydrogen bonding and electrostatic interaction. The experimental outcome showed that the nanohybrid sensor having 2.5% Au NPs exhibited detection limit of 33 ppm, higher response (14% @ 1000 ppm), faster response time (180 s) and excellent selectivity, which was attributed to the high surface energy of Au NPs and more adsorption sites for CO molecules. This study presents an exciting way of enhancing the gas sensing performance of a polymer by

Table 4
Literature survey on the sensing performance of polymeric/inorganic nanohybrids for hydrogen sulphide gas.

Sensing materials	Target gas	Conc.	Response	Response time (s)	Recovery time (s)	Operating temp. (°C)	Adv. Or disadv.	Ref.
$BaInSbSe_5$-G-PPy	H_2S	–	900–1400%	234	76	RT	High selectivity and sensitivity with outstanding reproducibility	Oh et al. (2021c)
Ch-IL-CuO	H_2S	100 ppm	217.9%	14.4	–	40	Extremely high sensitivity to H_2S gas	Ali et al. (2020b)
Ch-IL-WO_3	H_2S	100 ppm	187%	13.6	–	40	Highly selective, sensitive and long-term stabile along with low power consumption	Ali et al. (2020a)
CMC-IL-CuO	H_2S	300 ppm	20%	52.4	–	40	Decent responses and selectivity towards H_2S gas	Hittini et al. (2020)
PANI-WO_3-$CuCl_2$	H_2S	–	–	10	–	RT	High and fast response as well as an excellent selectivity to H_2S gas	Belkhamssa et al. (2021)
Ch-IL-MOF	H_2S	100 ppm	91%	<8	<30	RT	High sensitivity, low-power consumption and flexibility	(A. Ali et al., 2021)
PANI-SnO_2-RGO	H_2S	0.1 ppm	9.1%	–	–	RT	Flexible sensor, great stability and repeatability	Zhang et al. (2019a)

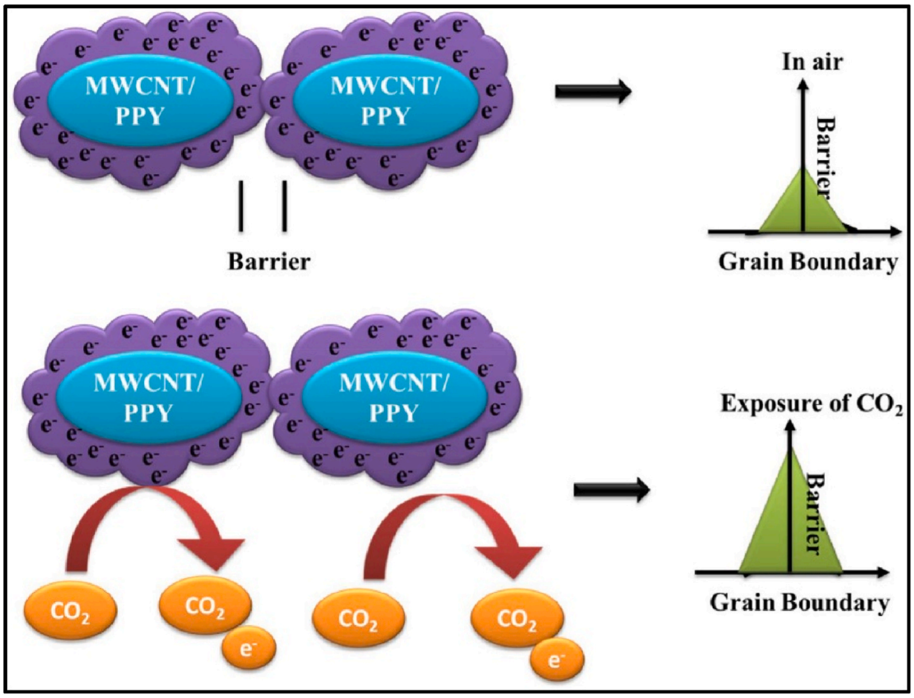

Fig. 10. Gas sensing mechanism of PPy-MWCNTs based nanohybrid sensor. Reprinted with permission from (Kumar et al., 2020).

incorporating a noble metal (Nasresfahani et al., 2020). Sensing performance of different polymeric/inorganic nanohybrids sensing of carbon oxides has been given in Table 5.

3.6. *Sensing of liquified petroleum gas*

Liquid petroleum gas (LPG) is highly flammable and produced during the processing of crude oil. LPG typically consists of a mixture of hydrocarbons such as butane and propane (Albaris and Karuppasamy, 2019). It is extensively used as a fuel in automobiles as well as for industrial and domestic applications. On the other hand, the Permissible Exposure Limit (PEL) has been stated as 1000 ppm for LPG (Patil et al., 2015). Similarly, due to its high flammability, even a small amount of LPG can cause a huge fire resulting in destruction of human life, property and infrastructure (M. Singh, Singh et al., 2021). Hence, there is a dire need to develop cost effective, compact in size, lower power consuming, selective and sensitive LPG sensor for household and industrial applications.

Ram and colleagues examined the effect of irradiation of low energy ion beam on the physico-chemical and LPG sensing features of PEDOT: PSS-WO_3 hybrid thin films (Ram et al., 2020). The composite solution was prepared by mixing 1 wt% or 5 wt% of WO_3 nanoparticles in

Table 5
Literature survey on the sensing performance of polymeric/inorganic nanohybrids for carbon oxides.

Sensing materials	Target gas	Conc.	Response	Response time (s)	Recovery time (s)	Operating temp. (^oC)	Adv. Or disadv.	Ref.
PANI-SnO_2-UV	CO_2	5000 ppm	47.4%	35.1	43.2	RT	Good reproducibility, dependability and selectivity response in multi-cycle towards various CO_2 levels	Nasirian (2020)
CuZnSnSe-G-PPy	CO_2	1000 ppm	65%	7–15	6–35	RT	Facile and low-cost route	Oh et al. (2021b)
LaNiSbWO$_4$-G-PPy	CO_2	1800 ppm	120%	<1	<1	RT	Good repeatability, reproducibility and measurement accuracy	Oh et al. (2021d)
PPy-MWCNTs	CO_2	1000 ppm	720 ppm	30	37	RT	Higher accuracy	Kumar et al. (2020)
PPy-CuPc	CO_2	5000 ppm	175%	34	175	RT	Low-cost, reliable and sensitive towards CO_2 gas	Riyazi & Azim Araghi (2020)
PANI-SnO_2	CO_2	5000 ppm	47.4%	35.1	43.2	RT	–	Nasirian (2020)
PANI-NaO_2	CO_2	4000 ppm	60%	900	600	RT	–	Barde (2016)
PANI-TiO_2	CO_2	1000 ppm	53%	552	342	RT	–	Sonker et al. (2016)
PANI-$LaFeO_3$	CO_2	5000 ppm	12.13%	197.82	42.17	RT	–	Karouei & Moghaddam (2019)
PANI-Au NPs	CO	6000 ppm	27%	180	200	RT	Low detection limit and good selectivity	Nasresfahani et al. (2020)
PANI-SnO_2-Pd	CO	–	30–401%	11–88	45–62	RT	–	Kishnani et al. (2021)
PDDA-MWCNTs	CO	20 ppm	11.5%	18	33	RT	Stable for 2 months with excellent reproducibility	Roy et al. (2020)

PEDOT:PSS conducting polymer. The hybrid films of PEDOT:PSS-WO_3 were deposited on the glass substrate via cost-effective drop casting technique (see Fig. 11a), which also possess silver electrodes to measure the sensing response of LPG at room temperature. The low energy ion beam was then used to irradiate the nanohybrid thin films (see Fig. 11b) either under ambient conditions or under vacuum. Silver paste was used to connect with the continuous surface of the hybrid films as shown in Fig. 11c, in order to monitor the sensing behaviour of hybrid film. The XRD results displayed a decrease in particle size by increasing the fluence of ion beam irradiation, which suggested the chain scission due to irradiation. The nanohybrid films irradiated at lower fluence displayed higher sensitivity and faster response times, which was attributed to lower surface defects. Therefore, this approach can be used to enhance the structural properties of composite sensors for different gas sensing applications at room temperature (Ram et al., 2020).

Singh and colleagues developed PANI-ZnO-Ru based nanohybrid through *in-situ* polymerization method and determined their LPG sensing behaviour at room temperature (RT) (M. Singh et al., 2021). The microscopic analysis showed the highest porosity for PANI-ZnO-Ru based nanohybrid, which facilitated its sensing behaviour towards LPG. Moreover, the nanohybrid sensor exhibited highest sensitivity (1.22) and lowest response and recovery times (28 and 45 s, respectively) as compared to ZnO and Ru-doped ZnO. The nanohybrid (PANI-ZnO-Ru) thin film was described as p-type material with holes as a majority charge carrier. Upon exposure to LPG, the composite sensor released the electrons from the nitrogen chains present in PANI. The atmospheric oxygen was then reduced by these electrons to create O^- ions on the surface of thin film and oxidized the butane molecules. The majority charge carriers of nanohybrid (i.e., holes) were then combined with the electrons, which eventually resulted in a decrease in the number of charge carriers and an increase in the resistance of the material. Upon removal of LPG gas, the resistance of the material decreased again due to the discontinuation of recombination process between holes and electrons. Hence, the presented material is a promising candidate for LPG sensing and, therefore, can be used to produce potential LPG sensors (M. Singh et al., 2021).

Thangamani et al. reported the synthesis of PVA-PPy-V_2O_5 nanohybrid film, having different concentrations of V_2O_5 nanoparticles, through solution casting method (Thangamani et al., 2021). The thermal analysis revealed an increase in the thermal stability of the nanohybrids by incorporating the nanoparticles. The strong chemical interaction between V_2O_5 nanoparticles and polymer blend (PVA-PPy) resulted in excellent mechanical properties of nanohybrid films (PVA-PPy-V_2O_5). The nanohybrid sensor having 15 wt% of V_2O_5 displayed the excellent selectivity, highest sensitivity (1.16%) and lowest response and recovery times (10 and 8 s, respectively) for 600 ppm of LPG at room temperature. This enhancement in gas sensing behaviour of nanohybrid film was attributed to the transformation of spherical V_2O_5 structures to nano-rods of V_2O_5 in the nanohybrid, which was verified by AFM and SEM analysis (Thangamani et al., 2021). This flexible chemiresistive sensor can be used for commercial applications because of its excellent sensitivity and higher selectivity towards LPG (Table 6).

4. Summary and critical overview

In this review, applications of different polymeric/inorganic nanohybrids in gas sensing system have been reviewed. Different polymeric materials including PANI, PEDOT, PSS and PMMA hybridized with different inorganic materials have been explored for their sensing efficacy for different toxic gases (i.e., ammonia, hydrogen, liquefied petroleum gas, carbon oxides, nitrogen dioxides, etc.). Composites of polymer with inorganic materials enhance the active sites, conductivity potential, selectivity and sensing capacity of sensors. Sensing mechanism of different nanohybrid for sensing of gases has also discussed in detail. Results showed that polymeric/inorganic nanohybrids are potential candidates for sensing of various gases in detection limit from ppb-ppm with fast response, less recovery time at different temperatures as shown in Tables 1–6 with reported literature. Nanohybrid based

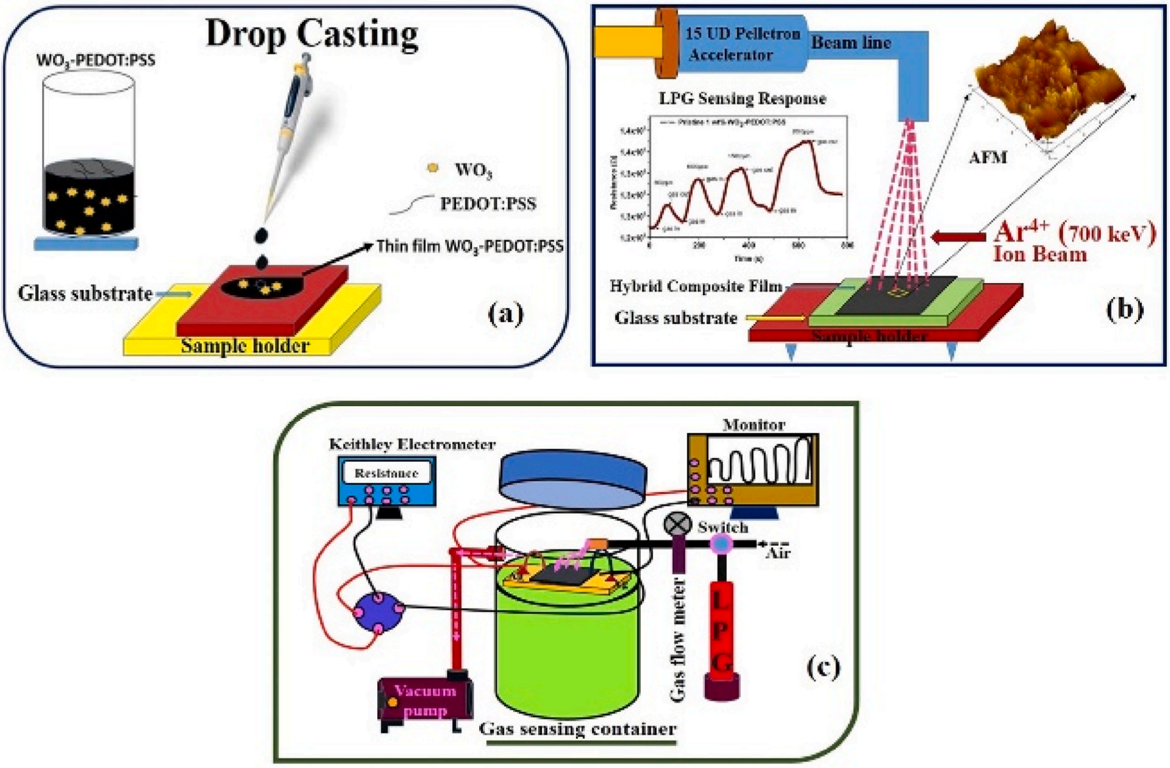

Fig. 11. (a) Schematic illustration of preparing nanohybrid thin films on glass substrate via drop casting technique; (b) Pictorial diagram of Ar^{4+} ion beam (700 keV) irradiation of hybrid nanohybrid film; and (c) The schematic demonstration of gas sensing setup. Reprinted with permission from (Ram et al., 2020).

Table 6
Literature survey on the sensing performance of polymeric/inorganic nanohybrids for LPG gas.

Sensing materials	Target gas	Conc.	Response	Response time (s)	Recovery time (s)	Operating temp. (^{o}C)	Adv. Or disadv.	Ref.
PEDOT:PSS-DMSO-PVA-SnO_2	LPG	100 ppm	79%	20	31	RT	Excellent conductivity, sensitivity, stability under mechanical deformations and humidity conditions (1–100% RH)	Almukhlifi et al. (2021)
PVA-PPy-V_2O_5	LPG	600 ppm	116%	10	8	RT	High sensitivity and excellent selectivity for LPG	Thangamani et al. (2021)
PANI-Ru-ZnO	LPG	–	–	28	45	RT	High sensitivity to LPG gas	(M. Singh et al., 2021)
PEDOT:PSS-WO_3-irradiated	LPG	1000 ppm	24%	25	40	RT	–	Ram et al. (2020)
PTh–ZnO	LPG	1200 ppm	55.7%	–	–	RT	Excellent LPG sensing capability even at higher temperatures	Husain et al., 2020b
PPy-Bi_2O_3–Ag_2O	LPG	500 ppm	–	50	70	348K	High sensitivity, selectivity and stability	Choudhary & Waghuley (2017)
PANI-TiO_2	LPG	–	43.2%	76	95	–	Good response	Moradian & Nasirian (2018)

sensors exhibited great sensitivity, reliability and selectivity towards analytes, even at low concentrations. The fabrication of gas sensors with nanomaterials is beneficial as smaller devices may be synthesized which may be easily portable and can be used for detecting gases in fields with accurate measurements. Compared to different gas sensors based on different polymeric nanohybrids as PPy-PB-TiO_2, PEDOT:PSS-AVNF, PVP-CuO and others, PANI based nanohybrids showed highest response for sensing NH_3 gas such as PANI-WO_3 nanohybrid showed response of 3400% at 100 ppm concentration (Fan et al., 2020). These PANI based nanohybrids showed high selectivity for NH_3 gas and these sensors showed great flexibility, high sensitivity, low LOD and reusability. High sensitivity may be due to the synergistic effect of two combined materials and also because of high conductivity of PANI. For sensing of hydrogen, PANI based nanohybrids (i.e., PANI-SnO_2-Pd and PANI-Sm_2O_3) also showed high response and great sensitivity (Pippara et al., 2021). Polymeric nanohybrids based on PPy showed high sensing potential for the H_2S (900–1400%) (Oh et al., 2021c), CO_2 (720%) (Kumar et al., 2020), NO_2 (4500%) (J. Zhang et al., 2020a) and LPG (116%) gases. PPy based sensors showed high response, great accuracy and outstanding reproducibility. Hence, by developing polymeric/inorganic nanohybrids based sensor, faster response and low measurement limit can be obtained. Conclusively, gas sensing nanohybrids are very beneficial for the safety of environment, and hence, there is still a need to focus further on their development by using variety of sensing materials of high potential.

5. Future perspectives

In this review, sensing potential of polymer/inorganic nanohybrids for different gases has been explored. Sensors showed good response, sensitivity and repeatability and reviewed sensors worked well at room temperature. There are still many challenges which are necessary to be resolved for development of nanohybrid based gas sensors. There is a need to explore the exact sensing mechanistic pathway to determine the potential of materials in different fields. Cost effective routes should be introduced for the synthesis of nanosensors for great performance at commercial scale. Sensing material should be stable enough under different conditions and should have a capacity to be used several times. These research results regarding gas sensors are still at the stage of lab research, and therefore, many studies are further required to bring relevant results at industrial scale. Literature review suggest that the detection limit may obtain till ppb level, but the response is not so high. Thereof, various studies are required to develop highly sensitive sensors. Further investigations are required to solve other problems related to the development of sensors possessing higher sensitivity such as: (i) humid atmosphere is observed to influence the sensor performance as compared to the dry air, (ii) molecules of gas enters inside the metal-lattice and initiates hysteresis phenomena, (iii) polymeric nanohybrids do not exhibit long term stability, (iv) room temperature response of polymeric nanohybrids is not ideal, (v) ratio of materials during synthesis process affects the sensing performance, etc. In future, following points needs to be addressed while choosing composite materials for polymeric/inorganic nanohybrids based sensors: large surface area, chemically stable, great conductivity, high moisture resistance, varying temperature range, great gas adsorption and desorption potential. From the reviewed literature, the following are the possible important directions to enhance the sensing features of gas sensors: (i) optimization of structure of composite sensors and mixture ratio to get high surface area, (ii) enhancing the active sites number to increase the sensitivity of sensor, (iii) selection of suitable catalyst with high catalytic efficacy and conductivity for chemical doping to enhance sensor response value.

Credit author statement

Ahmad Shakeel: Conceptualization, Visualization, Writing – original draft, **Komal Rizwan**: Conceptualization, Project administration, Writing – original draft, **Ujala Farooq**: Investigation, Formal analysis, Writing – review & editing, **Shahid Iqbal**: Supervision, Writing – review & editing, **Ataf Ali Altaf**: Formal analysis, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

PPy	Polypyrrole
PB	Prussian blue
TiO_2	Titanium dioxide
PANI	Polyaniline
GO	Graphene oxide
SnO_2	Tin oxide
GNR	Graphene nanoribbon
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate)
AVNF	Ammonium vanadate ($(NH_4)_2V_6O_{16}$•$1.5H_2O$) nanofiber
MoS_2	Molybdenum disulphide
PVDF	Polyvinylidene fluoride
G	Graphene
PET:NH_2	Polyethylene terephthalate (PET) fibers with amino group
MWCNTs	Multi-walled carbon nanotubes
NiO	Nickel oxide

h-NiO	Hollow Nickel oxide
Nb_2CT_x	Niobium carbide MXene nanosheets
SRGO	Sulfonated graphene oxide
$LaNiMoSe_2$	Quaternary semiconductor
SWCNTs	Single-walled carbon nanotubes
RGO	Reduced graphene oxide
PVP	Polyvinylpyrrolidone
WO_3	Tungsten oxide
V_2O_5	Vanadium pentoxide
$SrGe_4O_9$	Metal oxide semiconductor
$CuFe_2O_4$	Copper ferrite
PMMA	Polymethyl-methacrylate
SiNWs	Silicon nanowires
PTh	Polythiophene
$LiCuMo_2O_{11}$	Quaternary semiconductor
3D-NGF	Three-dimensional nitrogen-doped graphene-based framework
P3HT	Poly(3-hexylthiophene)
CeO_2	Cerium oxide
en	Encapsulated
LGS	Langasite
PBTTT	Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b] thiophene]
$Ti_3C_2T_x$	Titanium carbide
γ-PGA	γ-poly(L-glutamic acid)
Teflon AF	Poly(4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene)
ITO	Indium tin oxide
Sm_2O_3	Samarium oxide
$BaInSbSe_5$	Quaternary semiconductor
Ch	Chitosan
IL	Ionic liquid (glycerol)
CMC	Carboxymethyl cellulose
CuZnSnSe	Quaternary semiconductor
$LaNiSbWO_4$	Quaternary semiconductor
CuPc	Copper phthalocyanine
Au NPs	Gold nanoparticles
PDDA	Poly(diallyldi-methylammonium chloride)
PVA	Poly (vinyl alcohol)
PDA	Polydopamine
NFs	Nanofibers
PA66	Polyamide 66
GN	Graphite nanosheet
CdTe	Cadmium telluride;
P3HB	Poly(hydroxy-3-butyrate)
PTSA	para toluene sulfonic acid

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