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Review Article

Nano-structured gas sensing materials for ammonia detection with special emphasis on medical applications

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Ammonia, a highly toxic gas, known for its wide industrial usage, is now gaining importance as a biomarker for quite a few terminal diseases. Therefore, the quest for a sensitive and selective ammonia gas sensor is booming. A brief study on the importance and various sources of ammonia gas has been recapitulated in this review along with the elaboration of ammonia as a biomarker for clinical applications embracing renal and hepatic diseases. In addition, developments in nanotechnology-based ammonia sensors have been summarized in-depth, emphasizing metal oxide semiconductor (MOS) based, polymer-based, and carbon nanomaterial-based gas sensors. This review has brought into the limelight the importance of sensing very low concentrations of ammonia. The performance of a wide range of MOS, polymer, and carbon nanomaterial-based sensors has been summarized in minute detail which will help researchers in attaining a quick analysis of state of art sensors to meet the needs of their intended application areas.

Keywords: Ammonia, Gas sensor, MOS, Polymer, Graphene, Renal, Hepatic, Biomarker

1 Introduction

Ammonia (NH_3), an alkaline natural gas with a density lower than air, is colourless and bears a pungent odour. The normal atmospheric NH_3 concentration ranges from 1 to 5 ppb[1]. Because of strong hydrogen bonds between molecules and transferable hydrogen bonds, it is easily liquefied[2]. It has a variety of uses in explosive productions, fertilizers, and refrigerant coolants[3]. Petrochemical facilities, and various sectors of food processing industries, are also the places where NH_3 is used on a daily basis. It is also reported that ammonia can also be utilized directly in fuel cells with small alterations in internal combustion engines due to its greater octane (120 as compared to gasoline, which normally varies from 86 to 93)[4]. Nevertheless, ammonia is a highly hazardous gas and it can cause harm to our respiratory, excretory as well as to our digestive systems.

Ammonia detection is getting ever-increasing attention amongst researchers due to its widespread use and its potential for harm to humans and the environment. MOS gas sensors, conducting polymer sensors, surface acoustic wave (SAW) sensors, catalytic field-effect device based sensors, quartz crystal microbalance (QCM) sensors, pellistor sensors, fiber optic sensors, memristive sensors, and gas sensor arrays are popular types of sensors used for ammonia detection [1,2,5,6,7]. Ammonia is an important volatile compound that is produced due to human activity as well as natural reasons. Ammonification takes place utilizing a series of metabolic processes that breaks down nitrogen-containing chemicals from pure nitrogen sources like leaves or food from agriculture and animals or any dead organic matter, with the help of bacteria and fungi[8]. Ammonia emissions from domestic animals are estimated to reach a value between 20 and 35 Tg/year worldwide[9]. Combustion from both chemical plants and motor vehicles is another source of ammonia. The chemical sector produces ammonia, which is used in fertilizer manufacturing and refrigeration systems. Ammonia emissions from combustion total between 2.1 and 8.1 Tg/year[9].

Gaseous ammonia is also created when ammonium ions present in earth surface interacts with alkaline rainwater[10]. Commercial ammonia is largely produced by the technique invented by Fritz Haber and Carl Bosch in 1909 where the reaction of nitrogen and hydrogen is catalyzed by an iron-based catalyst at about 500°C and 300 bar [Eq. (1)][11]. The NH_3 produced *via* this method is used for fertilizers, medicines, explosives, and preservation.

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$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \ldots(1)$$

NH_3 molecule has a significant impact on the worldwide biochemical nitrogen cycle, as well as atmospheric processes that lead to particulate matter creation, climate change, health consequences, and long-term implications in the ecology[12]. Excessive NH_3 inhalation can harm human well-being since its poisonous and corrosive effects cause diseases to the most important organs in the human body like the kidney, lungs, stomach, etc. The Occupational Safety and Health Administration states that the upper limits of NH_3 inhalation in the case of people are 25 parts per million for 8 hours and 35 parts per million for 10 minutes[11]. By detecting and measuring biomarkers in exhaled human breath (such as acetone, ammonia, nitrites, hydrogen sulphide, etc.), a range of diseases can be identified [13-16]. For a very long time, problems with the liver, kidneys, and stomach have been linked to the body's elevated ammonia levels. Abnormal liver and renal activity raises blood urea nitrogen (BUN) levels, which causes an excessive amount of ammonia to accumulate in the oral and nasal cavity as well as in the skin [17,18]. Taking these risk factors into account, precise NH_3 gas monitoring can be said to be the need of the hour.

In recent years, numerous researchers have successfully developed various ammonia gas sensors with outstanding performances. For instance, Rath *et al*[19]. reported a poly(2-acrylamido-2-methyl-1-propanesulfonic acid) based ammonia sensor for non-invasive medical diagnosis that could detect ammonia in the range of 30 ppb to 1000 ppm even at high humidity (RH>90%). In another work, Maity *et al*. reported a textile-based lead-free halide perovskite (methylammonium tin iodide) ammonia sensor that could sense ammonia by both visual colour change methods and electrical readout at room temperature with ~85% sensitivity at 100 ppm gaseous ammonia[20]. Wang *et al*. reported a spray coated 3D origami paper based $Ti_3C_2T_x$ MXene/ gelatin ammonia sensor with a good response of 7% to 50 ppm of NH_3 with detectable concentrations ranging from 5–500 ppm, exhibiting great potential for a wearable sensor. Duy *et al*[22]. reported ammonia gas-sensing capabilities of light-activated porphyrin-coated V_2O_5 nanosheets that could detect upto 5 ppm ammonia at room temperature. Sibi et al[23]. reported humidity activated ultra-selective room temperature gas sensor based on tungsten doped MoS_2/RGO composites employing hydrothermal method with 1 ppm as the limit of ammonia detection with substantial enhancement in response characteristics. Feng et al[24]. reported a design of a real-time human breath testing device which is based on ammonia sensitive PANI/WS_2 gas sensor on flexible interdigited electrodes using drop casting method that could detect 100 ppb ammonia at room temperature under different bending conditions[24].

This review discusses the most widely used materials for ammonia gas sensors along with the importance of ammonia sensors as a biomarker for clinical application as well as various nanostructured materials reported by researchers for ammonia detection. The review concludes with deliberations on potential directions for future advancements in ammonia gas sensors.

2 Materials & Methods

The successful detection of ammonia levels has applications in varied sectors, such as medicine, environment, and food. Researchers are working towards the improvement of sensitivity, selectivity, operating temperature, response time, portability, cost, and power requirements of ammonia sensors in various applications.

Commercial ammonia sensors generally use MOS[25], polymer[26], graphene oxide (GO)[27] as the sensing materials, while other sensing techniques such as acoustic, calorimetric, gas chromatographic, and optical are also employed for ammonia detection[28-30]. Due to high manufacturing cost, low sensitivity and selectivity, short lifespan, and power needs of the existing sensors, alternative sensors using nanomaterials have been the choice over the past few decades[31]. This section of the review elaborates on the various ammonia sensors reported by researchers and the sensing principles used in most popular ammonia sensing materials: MOS, polymers and carbon based materials.

2.1 MOS based ammonia sensor

MOS-based sensors are quite extensively studied category of gas sensors over the last few decades and are popularly used to ascertain the presence of combustible gases due to their advantages such as excellent sensitivity, higher accuracy, greater durability, high-reliability, less expensive, faster response times, higher durability and ease of fabrication as compared to other existing technologies[32].

MOS materials in nano form are preferable for gas sensor fabrication because of their lower operating temperature, and favorable mechanical, optic, electric, catalytic and magnetic characteristics that can be easily engineered with doping materials[37]. Figure 1 depicts some nanostructures including nanoribbons, nanotubes, nanoboxes, dumbbell-shaped nanocomposites whose shapes and dimensions greatly influence the behavior of electrons in material responsible for gas sensing.

The n-type MOS materials SnO_2 and ZnO, being very stable, are also seen to be popular as gas sensors in different nano-structures too[38]. Apart from that, other metal oxides such as V_2O_5 nanosheets[39], TiO_2 nanocomposites[40], and nanostructured nickel ferrite ($NiFe_2O_4$)[41], are also used for gas sensing, including NH_3. Ammonia detection with MOS gas sensors has applications in many fields including the medical, agricultural, environmental, etc. MOS material also has great flexibility of modification by doping it with other metals/noble metals such as Pt[42], Pd[43,44], Au[45], Ni[46], etc., and other metal oxides to form composites such as nanostructured SnO_2:Zn films[47], ZnO and CuO composited graphene nanostructures[48], MoS_2 nanosheets -decorated SnO_2 nanofibers[49], CuO-SnO_2[50], noble metaldecorated composites[51], etc. to achieve a better sensing performance.

The mechanism of sensing ammonia gas using MOS material utilizes a reversible chemisorption interaction amongst the NH_3 and the active sensing layer.

When atmospheric oxygen comes in contact with the free electrons in the MOS sensing layer, it is reduced to oxygen ions (O^-, O_2^-, O^{2-}) based on different operating temperatures, which are then adsorbed on the sensing surface [Eq. (2)]. This oxygen ionosorption causes a band bending in the material and a depletion layer is formed [Fig. 2(a)]. Upon exposure to a gas, the MOS sensor's conductivity varies because of the chemisorption interaction amongst the analyte and oxygen ions adhered to the sensor's surface. Eq. (3) depicts the ammonia sensing mechanism in the MOS sensing layer (n-type)[52]. When exposed to ammonia the conductance of the n-type sensing material increases mainly because of the release of free electrons, which were engaged with oxygen ions, back into the sensing layer [Fig. 2(b)][53].

$$O_2(ads) + e^- \rightarrow O_2^-(ads) \quad \ldots (2)$$

$$4NH_3 + 3[O_2^-(ads)] \rightarrow 2N_2 + 6H_2O + 3e^- \quad \ldots (3)$$

2.2 Polymer based ammonia sensors

Ammonia is thought to deprotonate the polymer, causing an alteration in conduction[54]. Polypyrrole, polyaniline, and polythiophene have been the three most commonly used conducting polymers in the gas sensor sector as the active sensing layer over the last ten years[55-57]. Amongst the various types of operation techniques like conductometric,

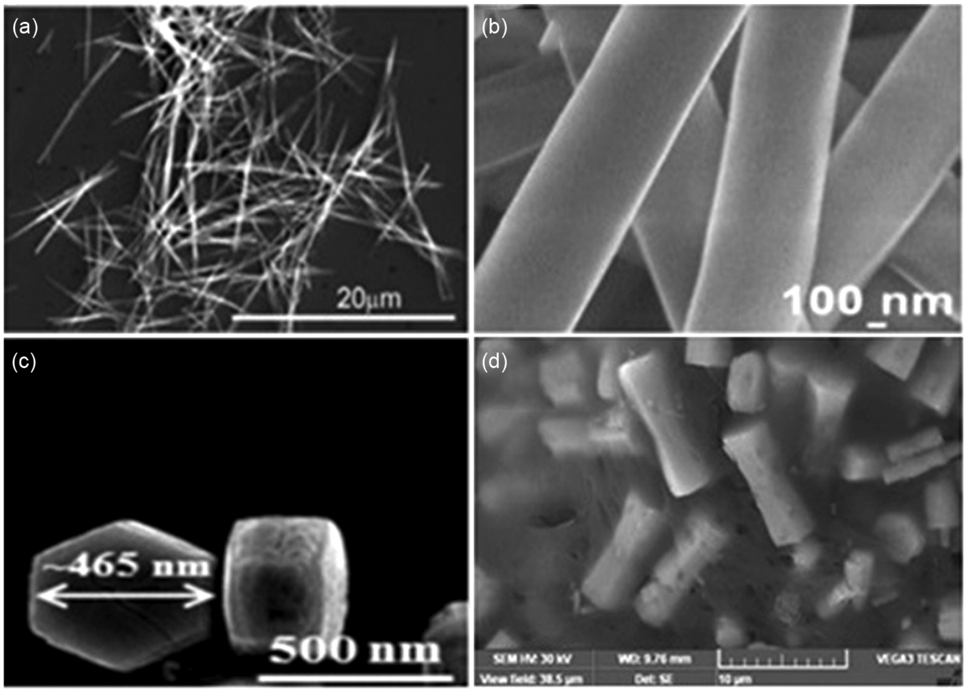

Fig. 1 — SEM images of different nanostructure MOS materials used for gas sensing applications (a) MoO_3 nanoribbons[33], (b) SnO_2 nano tube[34], (c) In_2O_3 hollow nanoboxes[35], and (d) micro-dumbbell shaped rGO/ZnO composites[36].

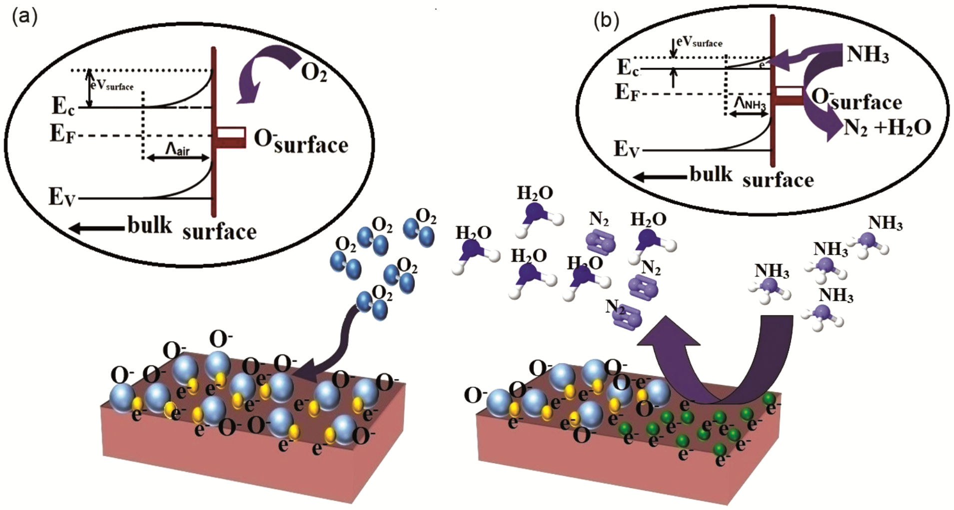

Fig. 2 — Ammonia sensing mechanism in a MOS material (a) Chemisorption of oxygen causing bend bending (inset) in air, and (b) Desorption of oxygen from MOS surface on exposure to ammonia gas and causing reversal in bend bending (inset).

potentiometric, amperometric, colorimetric, and others, the gravimetric mode is the most commonly used technique of operation for polymer sensors. The amperometric mode is used for a large number of conductive polymer gas sensors that employs a redox reaction to identify a particular gas that occurs between a target gas and a conducting gas.

The working of NH_3 sensing mechanism using polymer sensors is illustrated in Fig. 3. Polypyrrole films have a two-fold sensing mechanism based on (i) an irreversible reaction between NH_3 and the polymer material and (ii) NH_3 reversibly reducing the oxidized polypyrrole[58]. The reduction process changes the material's conductivity, which makes it appropriate for resistometric or amperometric sensing material for the detection of ammonia.

Polyaniline (PANI) is considered a stable conducting polymer. PANI can have various forms based on the state of oxidation. Leucoemeraldine (denoted as PANI-L) is a completely reduced form whereas pernigraniline (denoted as PANI-P) is a completely oxidized form and emeraldine (denoted as PANI-E) is a partially oxidized form of PANI. Researchers are mostly interested in the PANI-E form because of its excellent stability at RT and capability of being easily doped and converted into a semiconductive state[59]. Emeraldine base (PANI-EB), an undoped form of PANI-E is an insulator, whereas emeraldine salt (PANI-ES) is a doped form and a conductor. PANI-ES-based NH_3 sensor response is dependent on three factors: i) the exposure-induced balance of adsorption and desorption kinetics; ii) number of accessible NH+ sites on PANI-ES strand available for ammonia interactions; and iii) diffusion of NH_3 into PANI-ES[60]. Reactive-ion etching (RIE) is popularly used to produce a nano-structuralized PANI thin film for polymerization and spin coating. Morphology analysis, V-I characteristics, and XPS analysis showed that RIE with O_2 gas etching can significantly enhance the sensing region and also introduce an additional oxygen-containing diffusion pathway through hydrogen functional groups to absorb more NH_3 molecules[61].

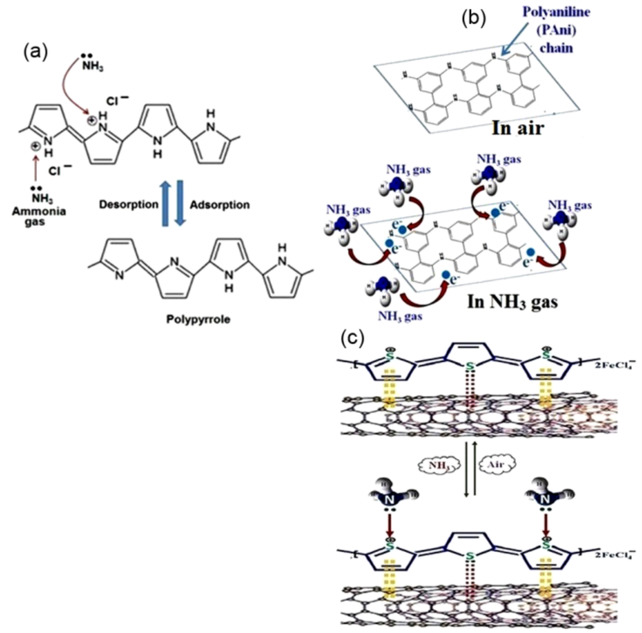

Fig. 3 — The NH_3 gas sensing mechanism for conducting polymers (a) PPy sensor[62], (b) PANI sensor[63], and (c) polythiophene/ MWCNTs nanocomposites[64].

The polythiophene based sensor's ammonia sensing depends upon the adsorption-desorption of NH_3 vapours on the surface of the sensor. Upon exposure, ammonia molecules primarily adsorb onto the surface and lone pairs on nitrogen atoms interacts with polythiophene polarons, which leads to polaron neutralization and a significant drop in electrical conductivity. Desorption of ammonia molecules in the ambient air results in an increase in conductivity with time[62-64].

Altering the structure of electronic polymer by doping is essential to produce a sensitive conducting polymer-based NH_3 gas sensor because it enhances the transfer of electron or hole and improves interaction with target gases. Nanostructures of conducting polymers is getting importance because of their higher surface-to-volume ratio (SVR) which in turn improves material-analyte interaction and analyte adsorption/desorption kinetics, causing enhanced sensitivity and rapid responses[65]. NiO/PPy hybrid nanostructures[66], PMVEA-doped PANI (PANI-PMVEA) nanostructures[67], are some of the modified polymer sensors with other materials for better response.

2.3 Carbon nanomaterial based ammonia sensors

During the last decade, there has been extensive scientific curiosity with graphene due to its unparalleled performance electrically, thermally, and optically, which are highly important for applications in sensors as well as in solid-state electronic device designs. Graphene, an allotrope of carbon and an atomically thin (semi)conducting material, has the potential to compete with metal oxides as a material of choice for microresistive gas sensors due to its low power requirements and excellent sensitivity to chemical analytes. Graphene has an extremely high SVR because each carbon atom is located on the surface and arranged in a hexagonal lattice nanostructure, making it exceptionally sensitive to adsorbed analytes[68].

Reduced graphene oxide, with p-type conductivity, serves as a donor in the RGO-NH_3 interaction and when exposed to the extensive area of pure graphene's surface, NH_3 molecule gets physisorbed. However, chemically synthesized RGO has functional groups and defect sites. In graphene-based sensing, a crucial part of the sensing mechanism is played by hydrogen bonds at defect sites involving functional groups which also includes physisorption of NH_3[69]. When NH_3 gas molecules (electron donor) are introduced to the graphene surface, they causes the Fermi level to rise by donating the weakly bonded electrons and approach the Dirac point. Here, the resistance increase is caused by donor electrons depleting holes in p-type graphene[70].

3 Results and Discussion

3.1 Ammonia as a biomarker for clinical applications

The volatile organic compound (VOC) concentration profiles during human exhalation correspond to a particular disease upon the presence of indicators such as ammonia in case of liver and renal disease, acetone in case of diabetes, dimethyl sulphide (DMS) in case of liver disease and fetor hepaticus, and isoprene in case of high cholesterol[71]. It should be noted that ammonia levels in breath in a healthy person are 0.278 ppm, while the same is 0.745 ppm in the case of liver disease and in between 1-5 ppm for renal disease[72]. Recent years have witnessed rapid advancement in noninvasive methods for quick and painless diagnosis of diseases. One such instrument is the breath analyzer which uses ammonia as a biomarker for the detection of many diseases by evaluating ammonia odor levels while exhaling. Intensified ammonia odor while exhaling results from unbalanced urea levels brought on by infection from the bacteria *Helicobacter pylori* in conditions affecting the liver, kidney, and stomach, and can be the primary breath biomarker for many disorders[73]. Biomarker concentrations in human breath, which are primary metabolites linked with the molecular configurations and metabolic activity such as regulation of cells, and tissues, as well as biofluids, have the potential to study disease progression. Fc@ZIF-8 is such an e-nose arrangement reported by Banga *et al.*[74] that uses ferrocene encased in a zeolitic imidazole structure to sense NH_3 levels in the breath. Figure 4 shows a 2D wearable gas sensor for monitoring health by exhalation that includes ammonia detection in graphene-based electronic textile (GES) which is a promising candidate for diagnosis in medical and healthcare applications[75].

3.1.1 Renal failure progression analysis using ammonia biomarker in human breath

Terminal ailment of the kidneys commonly known as chronic kidney disease (CKD) is a plight wherein the kidneys progressively decline its strength with time. The human exhaled breath in CKD patients is a urine-like odor called the uremic fetor due to the presence of excess NH_3 in breath created in the saliva as a breakdown product of urea. The metabolism of NH_3 in humans is illustrated in Fig. 5. The NH_3 in breath may originate from ammonia transport proteins located in the apical and basolateral plasma membranes of epithelial cells lining the respiratory tract. These proteins play an important part in kidneys in controlling the metabolism.

Patients undergoing peritoneal dialysis (PD), as well as before and during hemodialysis (HD) therapy, have higher ammonia concentrations in their breath[76]. Breath exhaled ammonia levels at the start of HD treatment are normally are found in between 1500-2000 ppb and decreased quickly throughout dialysis. Creatinine, plasma urea and NH_3 in breath were shown to have a good connection and can be useful in assessing the efficacy of dialysis[77].

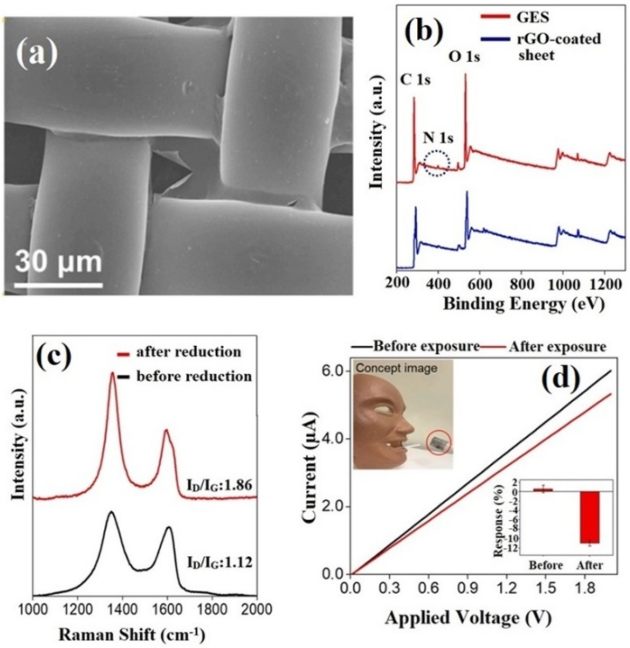

Fig. 4 — (a) SEM of GES, (b) the XPS of GES with rGO-coated structure, (c) The Raman spectra of the GES structure and (d) Electric current change of the GES after exposure to 10 ppm NH_3. The inset bar graph depicts the response change to ammonia[75].

Smith *et al.*[78], reported distributions of NH_3 in exhaled breath from the mouth, nose, and closed mouth of three healthy persons, wherein they concluded that as compared to the mouth, the median levels of ammonia in the nose are significantly lower, indicating that the mouth is the primary location of ammonia generation. This is most likely caused by the breakdown of nitrogenous matter by bacteria in the mouth and/or the enzymes in the saliva.

Numerous techniques are used to quantify breath ammonia, including cavity ring-down spectroscopy[79], photoacoustic spectroscopy[80], photonic crystal fiber[81], fluorescent breath ammonia sensor[82], and humidity activated ammonia sensor[83]. With a reported accuracy of 85%, the commercially available gas sensor TGS 2602 was utilized in a breath analyzer to analyze the mouth odour of ten applicants with renal failure symptoms and ten candidates without symptoms[84]. In addition to ammonia estimation, breath analysis in kidney patients can also help to estimate the total body water in them. Chronic kidney illness, at many times, has issues with an increase in total body water, which can result in an excess of extracellular fluid and the consequences that go along with it.

A. Shahmoradi *et al.*[85], designed and studied an NH_3 gas sensor using polypyrrole (PPy)/sulfonated graphene based composite nanomaterial for non-invasive ammonia detection in exhaled breath of HD patients (breath collected in a Tedlar bag of 1L). The

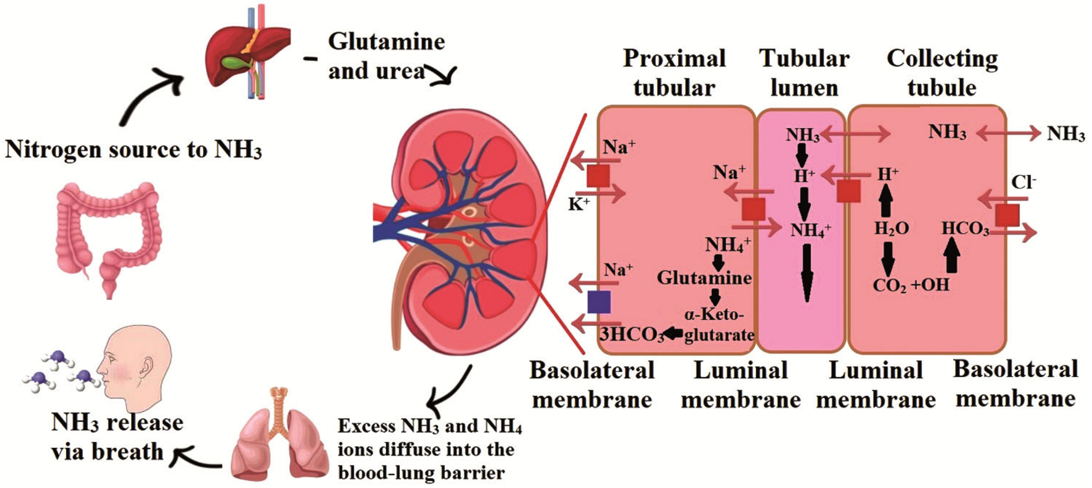

Fig. 5 — An illustration of the human body's ammonia metabolism and its source[76].

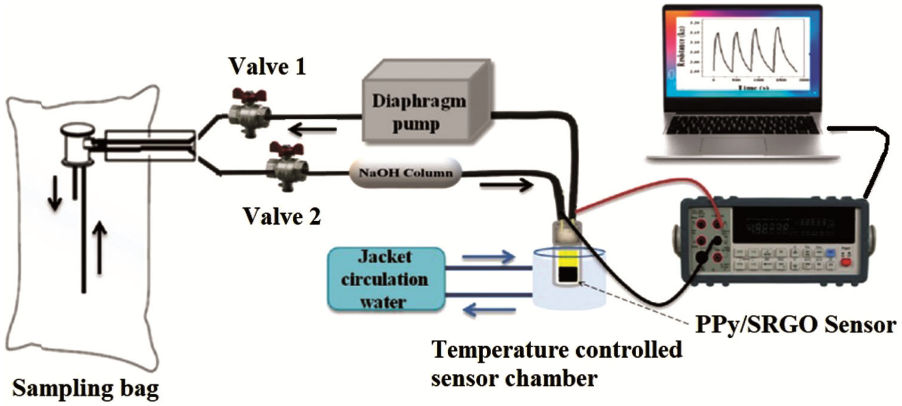

Fig. 6 — Breath analyzer system (Adapted with permission from[85]).

sensor could detect NH_3 at a concentration as low as 0.50 ppb at a temperature of 28 °C in exhaled breath of patients of average age 66 years undergoing regular dialysis. The result showed that HD can result in a 4-to-8-fold reduction in ammonia levels. They also showed a link between exhaled ammonia and BUN levels in HD patients. The schematic for ammonia sensing setup used is shown in Fig. 6.

3.1.2 Hepatic analysis using ammonia biomarker

Precise measurement of ammonia is crucial for clinical purposes since it is also a key biomarker to diagnose liver dysfunction. Ammonia levels is known to increase in case of any enzymatic problem or hepatocellular damage of the liver as prevents it from properly metabolizing the harmful substance, urea, in the body[86].

Measurement of breath ammonia may be helpful for hepatic encephalopathy diagnosis, therapy assessment, and follow-ups. In a study[87], in case of individuals with cirrhosis, blood ammonia and breath ammonia were found to be correlated. Ammonia levels in breath measured using ammonia electrode were found greater in cases of cirrhosis with hyperammonemia (0.997 ppm) as compared to that of without hyperammonemia (0.745 ppm). Ammonia levels in blood and breath both dropped as hyperammonemia was treated[87]. In another research[88] with 21 chronic liver disease (CLD) patients and 18 healthy individuals, it is found that breath ammonia is significantly high in case of CLD patients as compared to healthy people with Pearson's correlation p-value of 1.51×10^{-3}. To assure early identification and lower illness-related mortality, hepatocellular carcinoma (HCC) monitoring is crucial for at-risk groups. HCC, a common liver cancer, is the main cause of fatalities in individuals with CLD primarily due to late diagnosis and difficulties in treatment[89,90]. HCC is usually diagnosed using imaging techniques like CT and MRI along with blood tests to evaluate liver function. HCC is also known to be associated with the excretion of inorganic gases such as ammonia in breath, urine, faeces, or blood of patients and can be used as a biomarker for early detection of HCC[91].

Liver dysfunction diagnosis was also done employing an extremely thin Indium nitrite (InN) sensor with Pt doping with a minimum detection limit of 0.2 ppm, operating at 200 °C and a response time of 60 seconds when integrated with a silicone oil filter for selectivity enhancement[92]. This enables the device to be employed in the clinical area for non-invasive and targeted sensing of ammonia at sub-ppm level in exhaled-breath for investigating liver dysfunction. At 200 °C in presence of air, chemisorptions of O_2 molecules takes place on surface of InN epilayer to produce oxygen ions by attracting electrons from the conduction band (CB). When the sensing surface is exposed to ammonia gas, the oxygen ions interacts to release free electrons onto the surface, increasing the conductivity of InN epilayer (sensing mechanism is shown in Fig. 7).

3.2 Performance analysis of nanotechnology based gas sensors for ammonia detection

MOS materials in conjunction with graphene based materials are experimented widely for ammonia sensing and better performance is reported[93]. In a low concentration of 5 ppm ammonia, ZnO/CuO@graphene substrates exhibit improved sensing capability with a response time of 4.1 s and a purging time of two seconds [Fig. 8(a)]. Amongst other research works based on MOS material, a two-step preparation of a MoS_2/SnO_2 composite and its application as a room temperature (RT) (30° C)

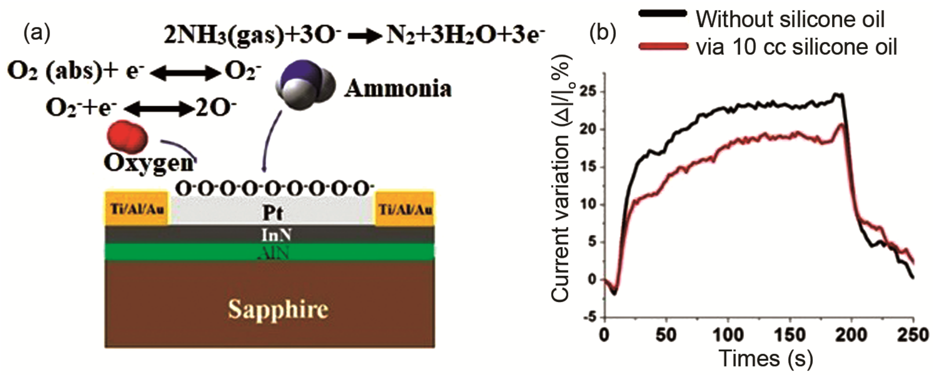

Fig. 7 — (a) Schematic of sensing mechanism of the Pt-coated InN sensor for ammonia gas, and (b) Response at 0.7 ppm NH_3[92]

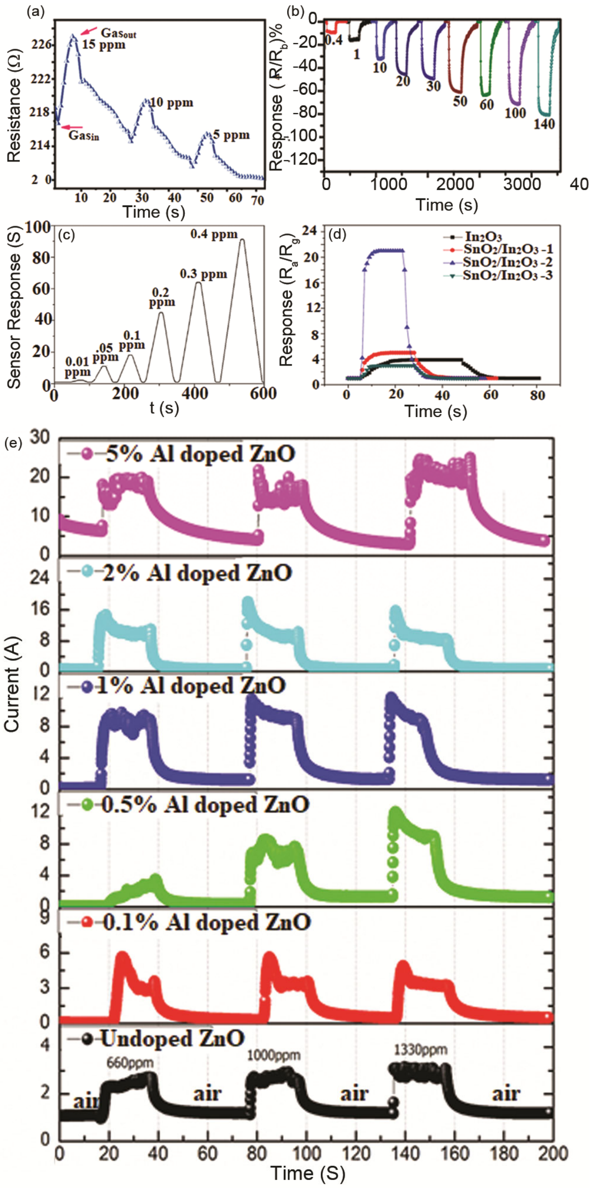

Fig. 8 — Response of (a) nanostructured ZnO/CuO@ graphene[93] (b) SnO_2/MoS_2 composite[94], (c) NiO[95], (d) SnO_2/In_2O_3[96], and (e) Al-doped ZnO based sensors for ammonia sensing[97].

ammonia sensor is reported of having 10% sensitivity even at 0.4 ppm ammonia including 2 s of response time and purging time of 10 s [Fig. 8(b)][94]. In another work[95], a simple way for fabricating a mesoporous NiO-based ammonia sensor having 91.2% sensitivity and response time of 54 s and purging time of 58 s for 0.4 ppm NH_3 at 25 °C is reported [Fig. 8(c)]. The mesoporous NiO sensor response remained stable even after 21 days. In another work[96], shown in Fig. 8(d), produces a comparative study of ammonia sensing using In_2O_3 nanofibre sensors and SnO_2/In_2O_3 sensors prepared via sol-gel and electrospinning respectively. In_2O_3 nanofiber sensors showed 16 s of response and 15 s of recovery time. However, SnO_2/In_2O_3 nanofiber sensors (16 at% SnO_2 in In_2O_3) have response time of 7 s and recovery time 10 s. SnO_2 coating can boost the response of In_2O_3 nanofibers towards NH_3 from 4 to 21 for 1 ppm NH_3. ZnO thin films doped with Al at 0.1%, 0.5%, 1%, 2%, and 5% synthesized using sol-gel method and deposited using a spin coater, exhibited their response towards NH_3 as shown in Fig. 8(e), where 5% Al-doped ZnO found to be the best amongst the sensors with other Al doping percentages[97].

Table 1 summarises the performances of a few more recent MOS-based ammonia sensors for applications in diverse fields produced using various fabrication approaches.

The response of polypyrrole (PPy) ammonia sensor towards wet NH_3 vapour in the range of 10 to 5000 ppm using camphor sulfonic acid (CSA) equipped with interdigitated electrodes(IDE) reported by Amini *et. al*[108] is presented in Figure. 9(b) It shows that the sensor resistance increases when the concentration of NH_3 vapour increases. Fig. 9(b) showcases the response of 2D Black Phosphorus(BP)/ Polyaniline (PANI) sensor as reported in[109]. Nanocomposite sensor's performance towards ammonia within 1 to

Table 1 — Performance summary of MOS-based NH_3 Sensors

Sl. No.	Materials	Dopants/ Composite	Morphology	Synthesis/ Fabrication method	Minimum Limit of detection (LOD) ofNH_3 Conc. (ppm)	Temp (˚C)	Response (%)/ Sensitivity (%)	Response time (s)	Recovery time (s)	Ref.
1	ZnO	Cr	Thin flake- shape with smallnanorods	Hydrothermal	10	RT	8.75 @50 ppm	270	300	98
2	V_2O_5	--	Nanosheets	Hydrothermal	0.4	RT	9.4% @5ppm	200	800	39
3	In_2O_3	Cr	HolllowNanobox	Oil bath	~1	140	11@10 ppm	1	18	35
4	WO_3	MoS_2	Nanosheets	Sonication	1	200	207	80	70	99
5	SnO_2	S	Nanoflower	Hydrothermal	2.5	RT	460@100 ppm	60	122	100
6	ZnO	Al	Nanoflower	Co-precipitation	1	RT	3.12	26	18	101
7	ZnO	Ti	Thin films	facile solution combustion	10.7	RT	34.7@100 ppm	91	198	102
8	$ZnSnO_3$	Au	Nanocubes	Hydrothermal	10	80	94.3@100 ppm	8	5	103
9	ZnO	Ni	Nanowire	SILAR	25	RT	5794	43	7	104
10	SnO_2	--	Semi-spherical microstructures and nanostructures aggregated on porous Si substrate	Spray pyrolysis	22.6	RT	175%@150ppm	18	86	105
11	Fe_2O_3	--	Thin film made of spherical, cubic, and rectangular cuboid shaped nanocrystals	Spray deposition	1	RT	46.5%@5 ppm	40	56	106
12	CuO	NiO	Nanoflakes	Drop casting	25	RT	31.74%@200 ppm	11.7	21.5	107

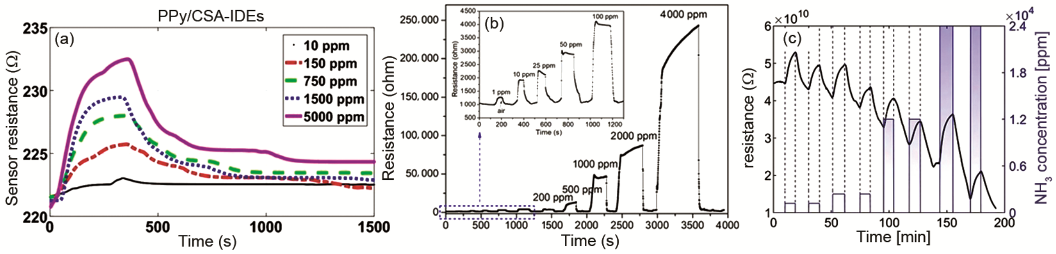

Fig. 9 — Response of the studied sensor at varied concentrations of NH_3 vapor designed based on (a) PPy/CSA-IDEs[108], (b) 2D Black phosphorus/polyaniline nanocomposite[109] and (c) $PThCF_3$[110] at RT .

4000 ppm range with response time of 28 s and recovery time of 46 s with a 76% change in resistance in NH_3 environment is reported. The composite is produced through oxidative polymerization of chemicals performed on-site and then deposited it onto interdigitated transducers (IDTs) and examined for 1 to 4000 ppm NH_3. Addition of BP to PANI can improve the surface area, also can get a unique trough shape for gas pathways, and produce p–π conjugation and p–p isotype heterojunctions, that in turn would increase BP/NH_3 PANI's sensing responses. Fig. 9(c)depicts the response of a sensing material based on substituted polythiophene for NH_3 sensing in gaseous and aquatic environments as reported by[110]. The increase in sensor resistance on NH_3 exposure can be possibly attributed to ammonia molecules interacting with p-type polymer backbones. Ammonia molecules can establish hydrogen bonds with PThCF3's polymer backbone and electronegative fluorine atoms. Two competing interaction processes cause reversible sensor response. Very low ammonium ion concentrations (10.0–79.4 l M) can be measured with 9% accuracy. Electrochemical sensors also responded to 10–1220 μmolL^{-1} ammonia in aqueous environment.

Table 2 lists the performance summary of some of the reported NH_3 gas sensors made of conductive polymers, operating at room temperature.

Carbon nanotude (CNT) are another attractive form of carbon based materials especially used for gas sensors fabrication. Analyte absorbed onto the surface of the CNT based sensing material can cause change in the conductance of the sensing material in three ways: Schottky barrier change at the junction of

Table 2 — Performance summary of conducting polymer-based NH_3 sensors at room temperature.

Sl. No.	Materials	Morphology	Fabrication method	NH_3 Conc. (LOD)	Response(%)/ sensitivity (%)	Response time (s)	Recovery time(s)	Ref.
1	Ag/Pani@MoS_2	Nanosheets made of spheres and tubes	hydrothermal, in situ polymerization	0.1 M	70.48 @1M	~45	~45	117
2	PAni-$CoFe_2O_4$	Clusters, porous and rough surface on the film	In situ oxidative polymerization	25 ppb	118.3 @50 ppm	24.3	~400	118
3	PANI-MWCNTs/PDMS	Film of nanoparticles and nanorods	chemical oxidation polymerization	10 ppb	11.8±0.2 @40 ppm	100	236	119
4	PPY-GO-WO_3	Granular Nanosheet	Spin coating	5 ppm	58	50	120	120
5	PANI	Thin film of nanofibre	Chemical polymerization	0.25 ppm	92 @ 100 ppm	59	145	121
6	POMA/V_2O_5	Thin films	chemical oxidation and Sol-Gel	20 ppm	800	60	1800	122
7	GCs/PANI	Nanospheres coated on hollow open-ended capsules	In situ oxidative polymerization	10 ppm	1.3	34	42	123
8	Pt/MoS_2/PANI	Nanoparticle clusters attached to surface of in-situ polymerized 3D nanoflowers	hydrothermal combined with in situ polymerization	250 ppb	16.64 @50 ppm	15	103	124
9	PPy/MXene	Layered structure	Hydrothermal	5 ppm	31.9 @100 ppm	38	383	125
10	PAni-CeO_2	Nanofiber	oxidative polymerization	10 ppm	80 @100 ppm	9.31	513.68	126
11	Butyric acid-doped polyaniline (BPANI)	Granular film	In situ chemical polymerization	50 ppm	513 @100 ppm	8.94	---	127
12	Polypyrrole	Nanoparticles	Polymerization	50 ppm	~82	120	120	128

electrode-CNT, transfer of electrons/holes between the CNT and analytes and increase in CNT-CNT junction distance[111]. CNTs exhibit p-type behavior at room-temperature. Exposure to reducing gases introduce electrons to CNTs' valence bands, thus, lowering hole concentration and conductivity. When electrons are removed from p-type SWCNTs, holes increase, resulting in increase conductance. Conductance may alter if scattering sites reduce CNT charge mobility. Absorption of analytes at the CNT-metal contact may change the Schottky barrier and conductance. Connecting multiple CNTs creates conducting channels because of their small length. If analytes are absorbed at intertube junctions, CNTs can change conductance.

The monitoring of significant environmental pollutants including NH_3, and other volatile organic compounds (VOCs), has been carried out successfully with the use of graphene[112-115].

It has been demonstrated that chemical vapor deposition (CVD) deposited pristine graphene can detect ammonia at the range of sub-ppm[116]. A sensor response of a graphene-based nanomaterial deposited on substrates of mica and SiO_2 for 500 ppm of ammonia at RT is shown in Fig. 10(a). It is important to note that more p-doping happens in graphene/mica than in graphene/SiO_2 substrate, and graphene/mica sensors are found to be more sensitive to ammonia as compared to graphene/SiO_2 sensors[116].

In another work[141], a graphene based sensor was reported which was fabricated by aerosol jet printing (Fig. 10 (b)). A highly selective ammonia gas sensor was reported using $SnTiO_2$@rGO/CNT nanocomposites, and the results are shown in Fig. 10(c)[129]. $SnTiO_2$@rGO/CNT nanocomposite was created using the solvothermal process with different Sn/Ti molar ratios of 1:10, 3:10, and 5:10. Enhanced NH_3 sensing performance of rGO/WS_2 heterojunction based sensor designed with marginal sulfonate decoration was reported which exhibited enhanced performance to 10~50 ppm ammonia concentration with response time of 100 s and purging time of 480 s at RT for 10 ppm NH_3 (Fig. 10(d))[142]. Incorporating sulfonate groups (S-O_3H) greatly improves desorption

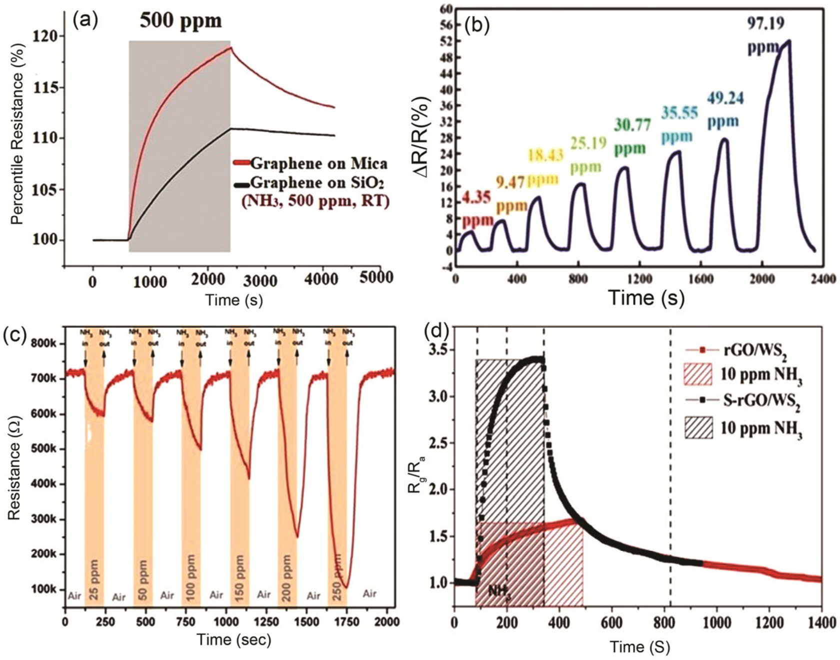

Fig. 10 — RT NH_3 sensor response (a) for 500 ppm using mica (red) and SiO_2 (black) as substrates[116], (b) Graphene sensor response deposited by aerosol jet printing[141], (c) Sn−TiO_2@rGO/CNT nanocomposites sensor response[129] and (d) rGo/WS_2 sensor with marginal sulfonate decoration[142].

Table 3 — Carbon based NH_3 sensors and their sensing performances.

S. No.	Materials	NH_3 con. (LOD) (ppm)	Synthesis/ Fabrication method	Tem. (˚C)	Response (%)/ Sensitivity (%)	Response time (s)	Recovery time (s)	Ref.
1	Sn−TiO_2@rGO/CNT	25	Solvothermal	RT	85.9@ 250 ppm	99	62	[129]
2	MoO_3/MoS_2/rGO	1	Hydrothermal	200	52 @100 ppm	30	4	[130]
3	WS_2/rGO	10	Hydrothermal	45	13	113	232	[131]
4	rGO/MoO_3	0.2	Hydrothermal	RT	32.44@ 5ppm	33	540	[132]
5	CeO_2/MWCNT	0.5	Two-step co-precipitation	RT	~6% @7 ppm	35	100	[133]
6	rGO/Cu_2O	0.005	Water bath heating	80	97@5ppm	1	1	[134]
7	rGO/PANI	0.05	In situ synthesis	RT	~486% @80 ppm	2.1	57.1	[135]
8	AuNP coated SWCNT	0.5	Sputtering	140	9.5%@1ppm	12	52	[136]
9	rGO/Co_3O_4	20	Solvothermal	RT	1.78@20ppm	351	~1200	[137]
10	rGO-Modified $ZnWO_4$/ WO_3	10	One-step calcination	140	10.1%@20ppm	80.1	261	[138]
11	Zinc doped MoS_2/RGO	6	In-situ hydrothermal	200	32.40% @40 ppm	21.3	44.90	[139]
12	rGO/NiO	20	Solvothermal	RT	4.14% to 100 ppm	290	166	[140]

capacity, and the newly inserted active acid centres make it particularly sensitive to ammonia molecules. Table 3 summarizes the performance parameters of a few recently reported carbon-based NH_3 gas sensors along with their fabrication methods.

4 Conclusion

Ammonia is an alkaline colourless natural gas, extensively used in explosive productions, fertilizers, refrigerant coolants, various sectors of food processing industries and petrochemical facilities. Detection of ammonia is getting ever increasing attention amongst researchers as it is a highly hazardous gas that can harm respiratory, excretory and digestive systems. Research on ammonia detection has also been attracting significant importance because of its use as biomarker for clinical applications especially for analysis of renal failure progression and hepatic analysis. The human exhaled breath in CKD patients has an odor called uremic fetor which is mainly credited by the excess NH_3 present in breath created in the saliva as a breakdown product of urea. Ammonia levels increases in case of any enzymatic problem or hepatocellular damage of the liver, hence, detection of breath ammonia progression becomes useful for hepatic encephalopathy diagnosis, therapy assessment, and follow-up. It is important to note that the concentration level of ammonia in exhaled breath at the early stage of terminal diseases like CKD and HCC are very low, which sprouts a detailed research in developing a low ppm ammonia sensor.

The most common types of sensors used for ammonia detection are MOS gas sensors, conducting polymer sensors, SAW sensors, catalytic field-effect device based sensors, QCM sensors, pellistor sensors, fiber optic sensors, memristive sensors, and sensor arrays. During the last couple of decades, researchers have opted for alternative nanomaterials-based sensors because of higher manufacturing costs, low sensitivity and selectivity, short lifespan, and power requirements of the existing sensors. Since MOS materials in nano form can easily be tailored to have desirable mechanical, optical, electric, catalytic, and magnetic properties, they are getting attention for the design of gas sensors because of their lower operating temperature. MOS-based sensor fabricated with facile hydrothermal self-assembly method reported have detected ammonia with sensitivity up to 94.3%. The importance of polymers-based ammonia sensors is growing as ammonia deprotonates the polymer, changing its ability to conduct electricity. A polymer gas sensor based on PANI-MWCNTs/PDMS using the chemical oxidation polymerization fabrication method reported ammonia sensing at a concentration of 11.8 to 40 ppm with sensitivity up to 90%. Carbon nanomaterial-based gas sensors have demonstrated unparalleled performance electrically, thermally, and optically. Graphene, an allotrope of carbon and an atomically thin semiconducting material has an extremely high SVR and is arranged in a hexagonal lattice nanostructure, making it exceptionally sensitive to adsorbed analytes. CNTs are another attractive form of carbon-based materials for gas sensing. CNTs exhibit p-type semiconductor characteristics at RT. Exposure to reducing gases lower the hole concentration and conductivity of the CNT-based sensing material. Various CNT-based nanocomposites are also reported to have good sensitivity toward ammonia. Ammonia sensors based on carbon-based nanocomposite material such as GO/$SrTiO_3$ fabricated using the chemical impregnation method were reported to have a sensitivity of up to 97.7%.

While advancements in sensing technology are promising, its widespread use in the clinical field for the diagnosis of disease is still years away. The validations of sensing results are still obligatory through simultaneous examinations employing traditional analytical techniques. Moreover, with non-invasive diagnostic procedures, the challenge of ensuring accuracy, stability, and calibration persists with various experimental setups. However, if researchers can develop a reliable and stable non-invasive detection system for accurately detecting terminal diseases, it will undoubtedly become the preferred technique for clinical diagnosis.

This review will connect the researchers working in the gas sensing sphere towards medical applications and assist in understanding the evolution and challenges of ammonia sensing, resulting in major advancements in the field.

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