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A systematic review on the detection and monitoring of toxic gases using carbon nanotube-based biosensors

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ABSTRACT

Environmental detection, monitoring and controlling of pathogenic or harmful gases has become an utmost priority. They contribute to major public health problems such as respiratory diseases, cardiovascular dysfunction and diseases, central nervous system (CNS) anomalies and other diseases (cancer, bronchiolitis, asthma etc.). Also, they are associated with frightening global warming thus affecting the ambient environment. Therefore, there is an urgent need to control and mitigate these gases. Notably, the existing conventional gas sensors are painstakingly very slow, labour and capital intensive, invasive and require specialized apparatuses and human capital to operate. A glowing need to develop cheap, fast, efficient, highly sensitive, portable sensors with less power usage and a high degree of reliability has been on the rise. Carbon nanotubes (CNTs) have been extensively explored to develop biosensors owing to fact that they are tubular-nanosized materials with excellent biocompatibility coupled with large surface area, excellent thermal, electrical, mechanical and optical properties. In the recent past, the invention and fabrication of CNTs-based biosensors and their mechanisms have been a subject of intense research studies in the detection and monitoring of gases. Therefore, in this short review, we present an in-depth overview survey of CNTs-based biosensors for gas sensing sourced from published papers and online articles. The paper also highlights challenges associated with CNTs-based gas sensors, possible remedial actions and future work opportunities in this research area.

1. Introduction

Air pollution remains one of the chief scourges in the world owing to its impact on climate change and human health that has led to a rise in morbidity and mortality rates. Human activities (anthropogenic) such as industrial processes, power stations, fuel engines, vehicles, ships, refineries, fertilizer applications and metallurgical processes coupled with natural activities like volcanic activities, breaking of rocks and minerals, the outbreak of forest fires, soil erosion and dust hurricanes are among the many factors that have vastly contributed to increased air pollution. Air pollution from anthropogenic activities remains the chief contributor to public health problems globally. It accounts for 9 million deaths per annum with 91% of the world population residing in areas where the air quality surpasses WHO recommended levels [1].

Contaminants and greenhouse gases such as carbon dioxide (CO_2), carbon monoxide (CO), ammonia (NH_3), hydrogen sulfide (H_2S),

Abbreviations: Words, Uncommon acronyms/abbreviations; Carbon nanotubes, CNTs; Permissible exposure level, PEL; Neurodegenerative diseases, ND; Nanomaterials, NMs; Single-walled carbon nanotubes, SWCNTs; Multi-walled carbon nanotubes, MWCNTs; Chemical vapor deposition, CVD.

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methane (CH_4), sulfur dioxide etc. have extensive effects on human beings which primarily depends on the length of exposure. For instance, short term exposure leads to chronic obstructive pulmonary diseases (COPD), coughing, breathing difficulty, respiratory diseases, wheezing and asthma. Whereas long term effects include cardiovascular diseases, chronic asthma, pulmonary insufficiency and cardiovascular mortality [2]. The extended exposure has equally resulted in neurological effects in adults and children with psychological problems like low birth weight, autism and fatal growth. Neurodegenerative diseases (ND) in another problem resulting from long exposure to air pollution. The mechanisms through which ND develops include oxidative stress, protein aggregation, inflammation and mitochondrial impairment in neurons (Fig. 1) [3]. Also, these gases have been linked to climate change which influences the topographical distribution of diseases as well as natural catastrophes causing devastating effects to the environment. For instance, global planetary warming can lead to the mutilation of plants, the melting of ice and iceberg, food shortage and the extermination of animals and people [4]. (See Table 1.)

Based on the aforementioned, environmental gas pollution is regarded as a global public health problem and interventions ought to be taken to mitigate the emissions. Efforts have been made and one of such is gas sensing technology which involves the use of sensors in monitoring and controlling the concentration. These sensors offer exciting features which include easy fabrication, low-temperature operation, both thermally and electrically stable and an elaborate wide spectrum of detection [11]. Based on properties, ordinary sensors can be grouped into electrical properties variation and physical properties variation. The former include metal-oxide (MO) semiconductors, polymers and all materials that can absorb moisture while the latter consists of methods such as gas chromography, infra-red (IR), calorimetric, optical and acoustic. The MO semiconductors have widely been used to develop sensors because of the ease with which constituent transition metals gets surface oxidation [12]. Examples of MO semiconductor sensors include TiO_2, NiO, ZnO, SnO_2 and CuO which have been successfully used in the detection of toxic gases. However, these MO have inherent disadvantages such as significantly high operating temperatures of more than 400 °C [13], ineffective detection of gases in low concentrations and difficulty in grain size limit values determination which have a serious effect on physisorption/chemisorption processes [14].

The advancement of technology has led to the realization of nanomaterials (NMs) such as carbon-based NMs (fullerene, carbon nanotubes, graphene, carbon dots etc.), gold nanoparticles (NPs), quantum dots (QD), metal oxide NPs etc. These NMs exhibit excellent properties such as large surface area (SA), great surface reactivity (SR), robust adsorption capacity and superior catalytic efficiency (CE) hence used as immobilization support for recognition molecules and aid in signal sensitivity enhancement during detection in electrochemical biosensors [15]. Specifically, compared to other carbon-based nanostructures, carbon nanotubes (CNTs) have been singled out as an ideal material for signal transduction in biosensors owing to their high degree of chemical stability, low residual current, readily renewable surface, faster electron transfer kinetics, enhanced currents and wide potential window [16]. Furthermore, their multi-walled nature, easy tunability and re-engineering of their structures coupled with a large surface area account for their potential in biosensing applications [17,18]. Their unique structure provides distinct electronic properties apt for signal transduction produced upon target/analyte recognition [19].

The CNTs are regarded as graphene sheets rolled up to form nanosized-tubes. They are composed of sp^2 hybridized carbons arranged in a hollow tubular shape with diameters of the range 1–100 nm and are grouped into two: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs can be viewed as rolled-up one-thick layer of graphene with a length of the order 1–00 μm while MWCNTs are formed of multiple sheets of graphene rolled-up to form tubes with a shared central axis and separation distance of 0.34 nm (Fig. 2) [17].

The CNTs structure influences their chemical, mechanical, physical and electrical properties. CNTs are mechanically strong and stiff owing

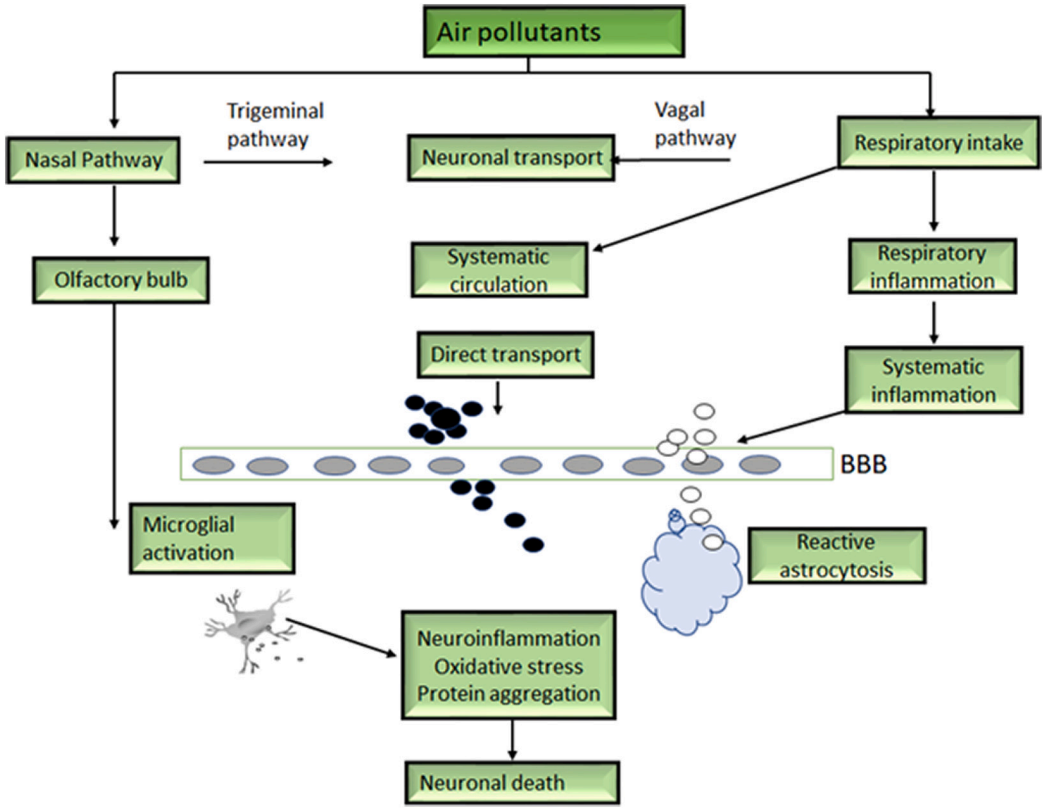

Fig. 1. Effect of air pollution on the brain via different pathways: Redrawn and adopted from [3].

Table 1
Toxic gases, their uses, primary sources, permissible exposure level limit (PEL) and their effects on human beings.

Toxic gas	Uses	Primary harmful sources	PEL	Effects	References
Ammonia (NH_3)	Its major usage as gas from refrigerators and similarly utilized in the industrial production of explosives, plastics, textiles	Agricultural activities: applications of fertilizers and animal husbandry	Total weight average (TWA) of 25–50 ppm (Occupational Safety and Health Administration-OSHA)	High concentration (500–1000 ppm) Causes immense nose and throat irritation. Lower concentration leads to eye, respiratory and skin irritation.	[5,6]
Nitrogen dioxide (NO_2)	Used as an inhibitor for polymerization, as a catalyst in oxidative RXN, for producing explosives and used as fuel for rocket	Combustion activities from chemical industries Vehicles fumes and other by-products	TWA of 5 ppm (OSHA)	Leads to Asthma and respiratory inflammations and diseases, causes coughs, wheezing and dyspnoea and pulmonary edema Long exposure may lead to a sense of smell impairment and lung-related chronic diseases. Formation of acid rain and photochemical smog.	[5,6]
Hydrogen (H)	Employed in the manufacturing of precise compounds such as hydrochloric acid (HCl), NH_3, as well as fuel for rockets and the lessening of cores of metals	Explosion centres, mining areas, petroleum sites.	TWA of 20 ppm of maximum 8 h (OSHA)	Causes dizziness, nausea, depression and vomiting. Exploding hence causing fire accidents. Loss of revenue due to spillage	[7,8]
Methane (CH_4)	Used as natural gases Also CH_4 can be utilized for generation of electricity, heating for buildings and burning waste in power garbage automobiles	Explosion centres, mining areas, petroleum sites.	TWA of 1000 ppm for a maximum of 8 h by the National Institute for Occupational Safety and Health's (NIOSH)	Exploding hence causing fire accidents Causes greenhouse effect Loss of revenue due to spillage	[7]
Carbon monoxide (CO)		Vehicle emissions Incomplete combustion of fuels and industrial emissions Smoking of tobacco.	TWA of 35 ppm of a maximum of 8 h (OSHA) and a maximum of 200 ppm for 5 min	This leads to CO poisoning by binding haemoglobin thus displacing oxygen. Causes headache, dizziness, emesis, cardio-arrest, unconsciousness, dysfunction of visual and hearing, vomiting. Disturbs greenhouse gases leading to water and soil temperature increase.	[9]
Hydrogen Sulfide (H_2S	H_2S has been habitually utilized for the manufacturing of Used to produce sulphuric acid as well as other inorganic sulphides	Release from natural gases, coal and petroleum factories/ refineries Decomposition of both animals and the human body remains	TWA of 10 ppm for 8-h exposure (OSHA)	Small concentration causes severe eye, nose, vomiting throat irritation. High concentration causes death, coma and convulsions.	[10]
Sulfur Dioxide (SO_2)	Used to produce sulphuric acid, sulfites and sulfur trioxide Used as disinfectant	Fossil fuels and industrial processes	TWA of 5 ppm for 8-h exposure (OSHA)	Cause lung diseases, irritation of respiratory system, production of mucus, bronchitis, bronchospasm, production of mucus, eye damage, skin redness and my lead to deteriorating of pre-existing heart diseases. Super corrosive and results in the formation of acid rain	[10] [2]

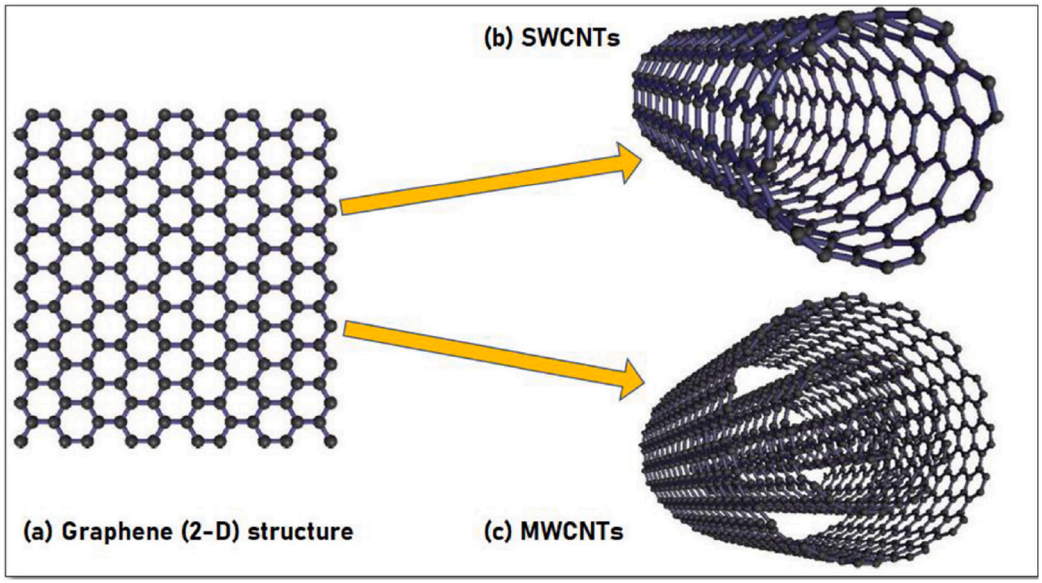

Fig. 2. Graphene layer rolled into (b) SWCNTs and (c) MWCNTs [17].

to the C—C bond with a tensile strength range of 11–63 GPa [20] and strengths of 10–100 times higher compared to the strongest steel [21]. They are thermally stable both in air and vacuum and exhibits a thermal conductivity of between 600 and 6600 $Wm^{-1}K$ which is two to fourfold higher than diamond [17]. Both MCNTs and SWCNTs show good metallic electronic properties with current densities range of 106–1010 A cm^{-2} and carrier mobility range of 20–104 cm^2V^{-1} s^{-1} [17]. Their one-dimensionality structure coupled with excellent electrical conductivity, high adsorption capability and magnificent bio-consistency has ensured a flow of high currents with minimal heating [22]. Also, the quasi-1-dimension property guarantees strong resonance Raman scattering (RRS), elevated optical absorption together with photoluminescence in the Near Infra-Red (NIR) range thus suitable for both in vitro and in vivo biological imaging [23].

The unique and excellent properties of CNTs have potentially seen these materials leading in biosensor applications in environmental monitoring toxic gases [24,25] with other wide range of applications being in solar cells [26], field emission (FE) devices [27], microwave absorption (MA) [6,7], electromagnetic interference shielding [28], fillers/reinforcers in fiber composites [29] batteries [30]. The properties of CNTs can further be improved through functionalization which can result in a permanent or reversible change of chemical properties and creating novel functionalities. This review reports on the use of CNTs-based biosensors in the detection/monitoring of toxic gases. The review starts with the introduction, the synthesis of CNTs, functionalization of CNTs, CNTs as biosensors, and applications of CNT-based sensors for gas sensing and conclusion and future prospects in the area.

2. Synthesis of CNTs

Ever since the discovery of CNTs, the synthesis and fabrication of CNTs have evolved due to technological advancement resulting in improved properties and yields. The commonly used methods; arc discharge (AD), laser ablation (LA), chemical vapor deposition (CVD), plasma torch and liquid electrolysis produce CNTs of different electrical, thermal and mechanical properties thus affecting or dictating their applications. Equally, the quantity of yields and purity of CNTs produced differ with each synthesis technique with emphasis put on best synthesis practice which offers negligible impurities and desirable chirality. The tube length is another parameter that is dependent on synthesis techniques and governs their applications [17]. The chart (Fig. 3) shows the commonly used methods to synthesis CNTs while Table 2 describes the four synthesis methods, their advantages and disadvantages.

The CVD method is regarded as a superior synthesis technique as proven by the advantages it has over other methods as enlisted above and it has been used quite extensively in the synthesis of CNTs. For example, Mohajeri et al. [32], synthesized vertically aligned CNTs utilizing stainless steel substrate under the thermal CVD method. This was achieved using a nanosized thin layer of cobalt as a catalyst and electrodeposited under a potential of −1.1 vs SCE on a substrate. As shown in Fig. 4a, CNTs of diameters ranging 150–200 nm and closed at both ends were produced. The use of high density of cobalt as catalyst produced bamboo-like nanotubes with a vertical alignment and fairly homogeneous distribution (Fig. 4b). The EDX analysis (Fig. 4c) revealed that the CNTs synthesized were mainly constituted of carbon and the growth occurred from the closed-end tubes. The presence of cobalt was explained to indicate that the mechanism in which the tip grows occurred due to the detachment of the catalyst NPs from the CNT surface during growth.

Equally, Xu et al. [33] used floating catalytic chemical vapor deposition (FCCVD) synthesis to investigate the role of iron (NPs) on CNTs growth in the gas phase and on a substrate along the reactor axis as shown (Fig. 5). The result showed that iron NPs were formed and grew at a temperature above 750 °C then the growth was terminated after carbon layers were encapsulated. This is the homogenous nucleation mechanism in the gas phase that resulted in the formation of NPs of 4–12 nm and the growth stopped thereafter because of carbon encapsulation. The other formation mechanism is heterogeneous nucleation where NPs of 20–35 nm was formed on the substrate which can be utilized as catalysts to form vertically aligned CNTs. The results showed that for the growth of CNTs on the substrate, homogenous nucleation cannot be considered as a precondition. Therefore, the research is very useful in achieving control of catalytic nucleation of NPs during CNT growth under the FCCVD method.

Also, MWCNTs were synthesized by catalytic CVD on Si substrate in a tubular horizontal reactor using acetylene as a carbon source. The synthesis temperature range was between 500 and 700 °C and a natural catalyst nontronites together with synthesized hematite were used. It was observed that the best quality of MWCNTs was produced at the highest temperature and depending on the catalyst used, bamboo-like

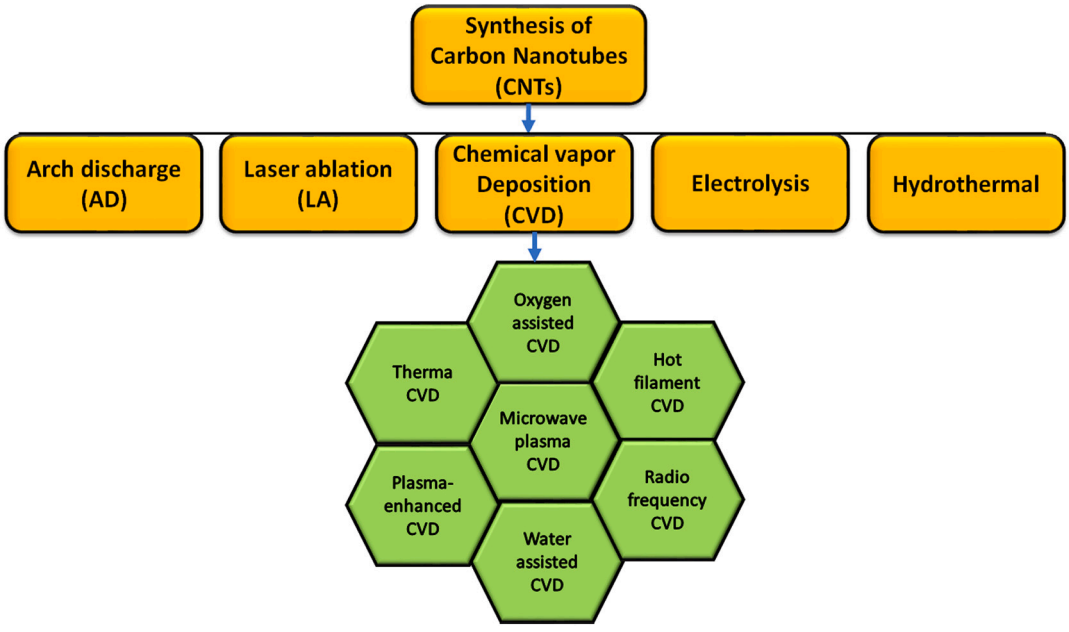

Fig. 3. Chart of the common synthesis techniques for CNTs.

Table 2
Synthesis methods, mechanisms of synthesis, advantages and disadvantages.

Synthesis technique	Mechanism of synthesis	Advantages	Disadvantages	References
Arc discharge	It was the first method used to synthesize and grow CNTs. The process happens in an evacuated chamber with two electrodes made of carbon thus acting as a carbon source. High temperatures above 1700 °C and low pressures of between 50 and 700 mbar are required. A supply of helium (or any inert gas) gas is then used to ensure an increased deposition of carbon. An application of a high DC-voltage between the electrodes produces inert gas-plasma which is essential for the evaporation of carbon atoms. The method grows both MWCNTs and SWCNTs with the latter requiring catalyst for growth.	Simple to implement and operate	CNTs produced are of poor quality as they are mixed with other carbon compounds CNTs produced requires a complex purification process Lacks control of chirality. Produces short tubes Requires high temperatures between 3000 and 4000 °C for evaporation of carbon.	[17,31]
Laser ablation	This technique uses the laser to ablate (disintegrate) the carbon target in a furnace under the flow of inert gas. The synthesis requires a catalyst and the formed CNTs are deposited on a substrate cooled externally with water.	Higher yields compared to arc discharge	Expensive to assemble and operate due to the use of expensive lasers. Not easy to scale-up CNTs mixed with metallic impurities CNTs formed are branched Requires high temperatures between 3000 and 4000 °C for evaporation of carbon.	[17,31]
Chemical vapor deposition (CVD)	The source of carbon in this technique is gas hydrocarbon. The hydrocarbon (CH_4, C_2H_2, or C_2H_4) molecules flow in the chamber and are broken down into small reactive masses at temperatures of 550–1000 °C. Under pressure and in the presence of a catalyst the small reactive carbon masses react with the catalyst mounted on the substrate to form CNTs.	The technique allows for scalability to enable large yields of CNTs The catalyst is not necessary since CNTs is not necessary since CNTs can be grown on semiconductors and stainless directly. allows control of the structure Different forms of hydrocarbon	High cost of assembly Require skilled personnel to operate	[7,17]
Liquid electrolysis	It involves the use of molten salts to produce CNTs. Through electrochemical reactions, the ionic salts are used in the decomposition of CO_2 electrolytically.	Very simple Easy to control during the synthesis process Easy to monitor and control structure and morphology Consumes less energy.		[17]

tubes, which exhibited curly shapes and straight individual bundles were synthesized. The nanotubes were found to have outer diameters of between 40 and 150 nm and lengths of tens of micrometres. A recommendation of the use of sodium forms of natural nontronites as catalysts was made because it is less costly and produces good quality graphite layers with a good structure for MWCNTs [34].

While the synthesis of a few-walled carbon nanotubes (FWCNTs) based on catalytic CVD using Ni—Mo and Co-MO alloys was performed in this study. The Polyoxomolybdate $Mo_{12}O_{28}(\mu_2\text{-}OH)_{12}\{Ni(H_2O)_3\}_4$ and $Mo_{12}O_{28}(\mu_2\text{-}OH)_{12}\{Co(H_2O)_3\}_4$ clusters were used as a source of catalyst. The decomposition of these clusters in air produced $NiMoO_4$ and $CoMoO_4$ coupled with MoO_3 phases and heating in the hydrogen atmosphere converted these phases into Ni—Mo and Co—Mo. These alloys were used as catalysts in the CVD synthesis of CNTs using ethylene as a source of carbon. Fig. 6a shows the TEM and EDX images of CNT that shows two encapsulated metallic NPs situated near the tube end and differentiated by composition. The EDX illustrates that the nanoparticle located at the tip of CNT is truly a Ni—Mo alloy with a richness of Ni while the one located at the cavity is composed of Mo with a blend of Ni which confirms that the growth of CNT was associated with these NPs. The CK-edge NEXAFS spectra (Fig. 6b and c) shows the walls of CNTs are well-graphitized and contains an only inconsequential percentage of oxygen-containing surface species/groups. These two metal-catalysts occasioned a large-scale synthesis of non-bundled, narrow and high purity FWCNTs [35].

3. Functionalization of carbon nanotubes (F-CNTs)

The chemical inertness coupled with the presence of robust $\pi - \pi$ interactions and stiffness contributes to the hydrophilic property of CNTs hence becoming insoluble in water and common solvents [17]. The CNTs forms an agglomeration with each other due to van der Waals forces resulting in difficulty in dispersion. It has been reported that 50 to hundreds of as-grown pristine CNTs agglomerate due to these forces leading to reduction of electrical and mechanical properties when compared to theoretical/simulated values of single CNTs [36]. The great task is not only on how to engineer these materials to dissolve in common solvents but also to disentangle individual CNTs and avert re-agglomeration. The problems can be resolved through the functionalization process which entails the physical or chemical attachment of unique molecules and functional groups to the ends or walls of CNTs. Functionalization has turned out to be a precondition for the facile assembly of nanosized CNTs-based devices. The functionalized CNTs becomes less toxic, easily dispersible and develop good biocompatibility [37]. The CNTs can be functionalized through exohedral functionalization or endohedral functionalization. The former is divided into covalent and non-covalent while the latter includes filling of CNTs from melted phases and filling of CNTs through solutions [19]. The exohedral functionalization is the most commonly used method and therefore, the following section covers the covalent and noncovalent functionalization.

3.1. Covalent functionalization of CNTs

Covalent functionalization of CNTs is realized in two ways; (i) by directly adding functional groups or active species to the sidewalls of CNTs (ii) attachment of modified functional groups at the nanotubes ends. The oxidation process is the most common method employed to functionalize CNTs thus ensuing in the creation of carboxyl groups (-COOH) on the surface of CNTs. The -COOH group create ester and amide bonds which permit molecules to covalently couple. Through acid treatment of nitric acid (HNO_3), the CNTs are refluxed and then exposed to a mixture of H_2SO_4 (1:3) for a maximum of 6 h under high power sonification (Fig. 7a) [38]. It has been demonstrated that functional

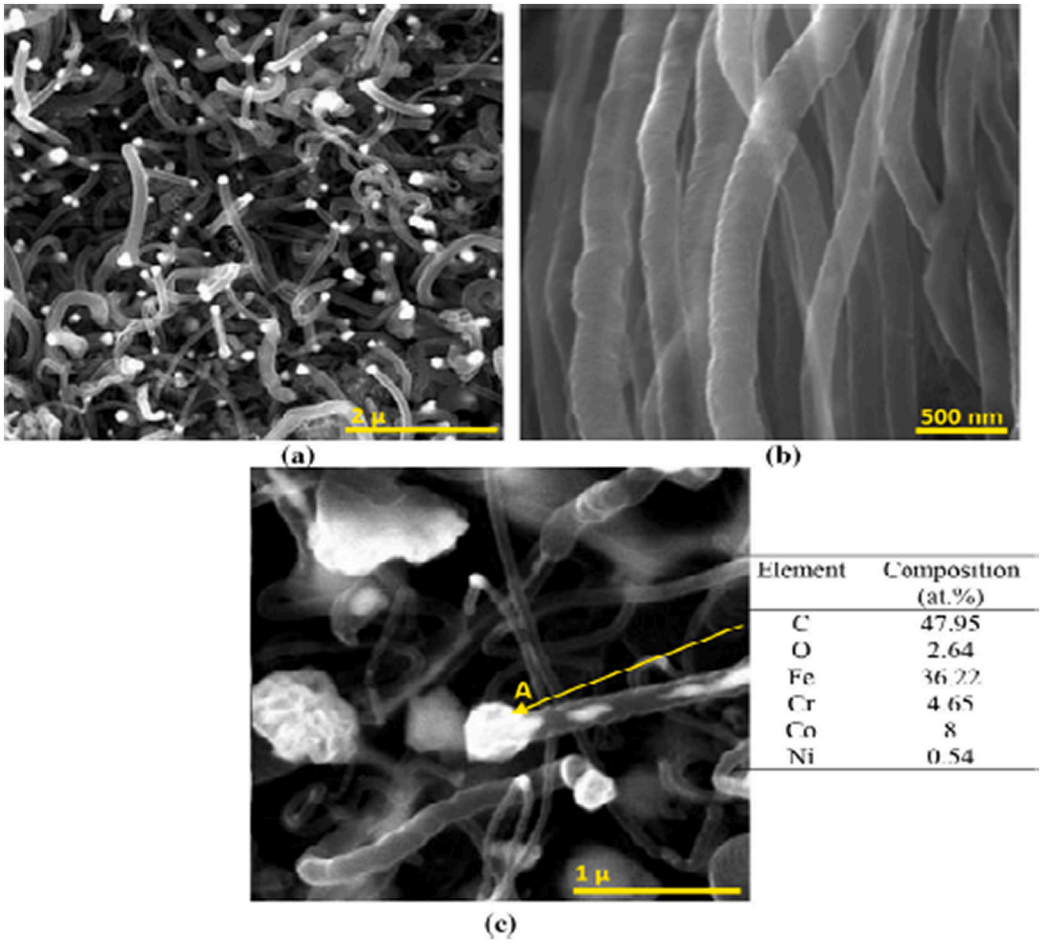

Fig. 4. SEM images of CNTs grown under the thermal CVD method [32].

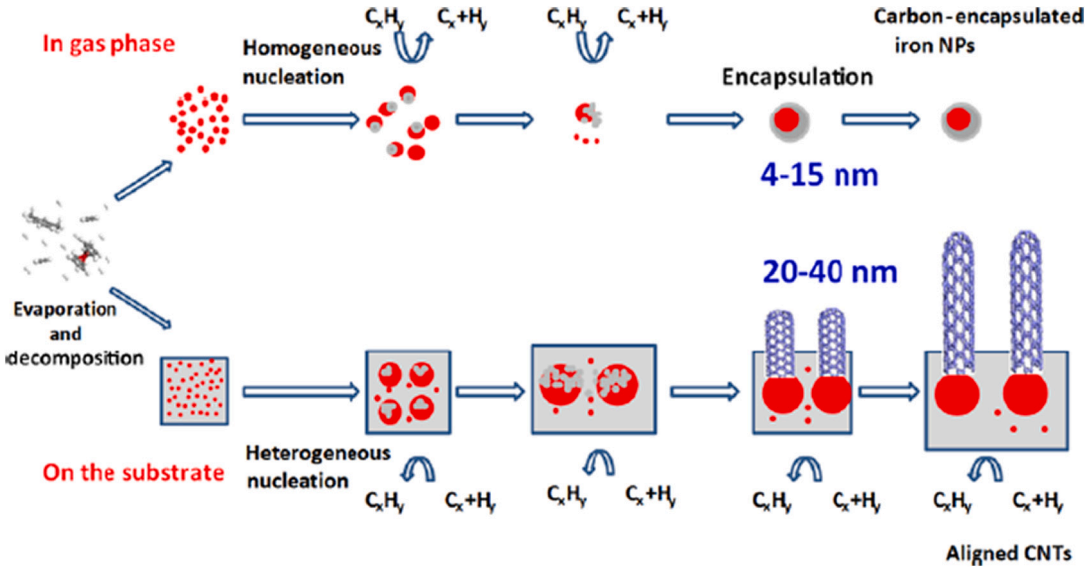

Fig. 5. Model for NP formation during CNT growth on a substrate under FCCVD method [33].

groups attached covalently to CNTs change the hydrogen bond by reducing van der Waals interactions of individual CNTs thus helping in nanotube segregation and solubility [39].

Equally, these groups allow the immobilization of other biomolecules on the surface of CNTs. For instance, carbodiimide compounds can react with carboxylated CNTs to activate the -COOH group which can directly react with amines in biomolecules. The N-ethyl-N′-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) which is mainly used water-soluble carbodiimide reacts with the COOH group to produce an intermediate *O*-acylisourea ester that can be

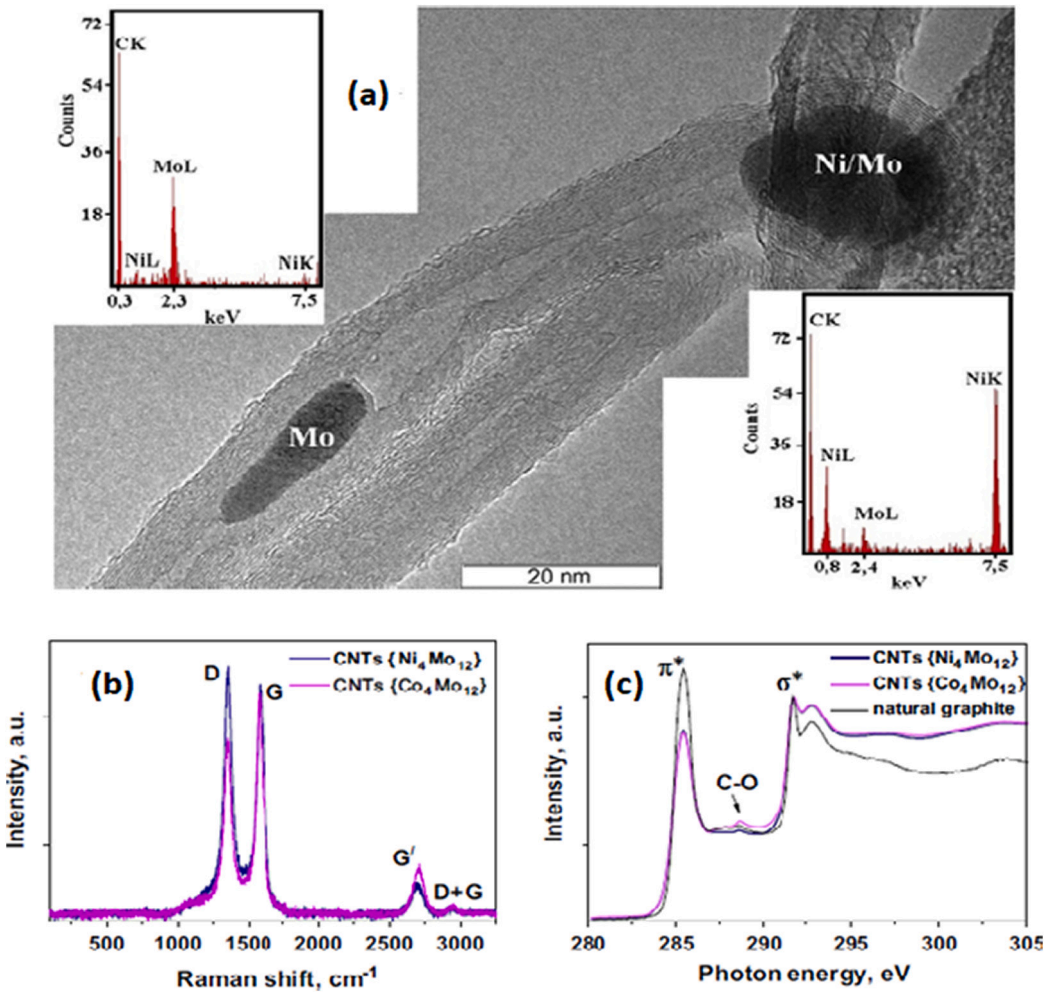

Fig. 6. (a) TEM and EDX of FWCNTs (b) Raman spectra of CK-edge NEXAFS (c) Raman spectra of FWCNTs using Ni—Mo and Co—Mo as catalysts [35].

displaced easily by primary amine [15]. However, if there is a formation of defects on surfaces of functionalized CNTs, chemical chains and reactive organic groups are bound to react in these sites forming more defects which can result in the weakening of thermal, electrical and mechanical properties [40]. Also, functionalization by oxidation leads to the destruction of structure which includes thinning and shortening of CNTs with the production of carbonaceous debris [41]. Liu et al. have equally reported a reduction of both photoluminescence and Raman scattering of SWCNTs through covalent modifications [42].

Apart from oxidation, photochemical and electrochemical functionalization have emerged as other forms of covalent functionalization. In the former, photoirradiation has been employed to produce reactive species like nitrenes during the sidewall reactions (Fig. 7b) [41]. While in the latter, an application of constant potential or current is made to the CNT electrode which is immersed in a solution having an appropriate reagent (Fig. 7c). Very reactive species are generated by the reagent owing to the electron transfer emanating from the reagent and CNT. For example, electrochemical reduction of aryl diazonium salts was used to produce small-diameter nanotubes. It was found that the nanotubes derivatized with 4-tert-butylbenzene moiety possessed enhanced dispersion in organic solvents [43].

Biosensors fabricated from covalently functionalized CNTs have demonstrated the ability to detect and analyse real samples. For instance, an amperometric sensor fabricated by copper nanoparticles immobilized on covalently functionalized MWCNTs modified glassy carbon electrode (CuNP/f-MWCNT/GCE) has been devised for H_2O_2 detection. The detection revealed a concentration of 32.8 (3.1) compared to 33.6 (4.3) % (*w*/w) of the standard method thus showing a good agreement of 97.6% of the results [44]. Similarly, an electrochemical biosensor for sensing hydrogen peroxide (H_2O_2) has been devised covalently by immobilizing horseradish peroxide (HRP) on modified MWCNTs by $\gamma-$ aminobutyric acid (GABA) on glassy carbon electrode. At the pH of 7.0, the cyclic voltammograms of the enzyme film exhibited quasi-reversible redox peaks according to the Fe(III/II) redox process of HRP with the biosensor showing good efficiency of detecting H_2O_2. The heterogenous electron transfer rate, surface coverage and Michaelis-Menten constant of immobilized HRP was determined to be 1.11 s-1, 3.029 $\times$ $10^{-9} mol\ cm^{-2}$ and 0.23 mM respectively. The biosensor showed high reproducibility, stability and repeatability [45].

3.2. *Non-covalent functionalization of CNTs*

Noncovalent functionalization modifications are anchored on interactions involving the hydrophilic section of the adsorbed molecules and the sidewalls of CNT via p-p, CH-p and van der Waals among other interactions and the hydrophilic part offers solubility in common solvents. The noncovalent functionalization is advantageous over covalent since many functional groups can be added to the surface of CNTs without compromising the p-system of the graphene layer hence preserving the chemical and physical properties of CNTs (Fig. 8 shows the comparison between covalent and non-covalent) [41].

Non-covalent functionalization can be obtained through various interactions namely; through $\pi - \pi$ interaction (where aromatic molecules

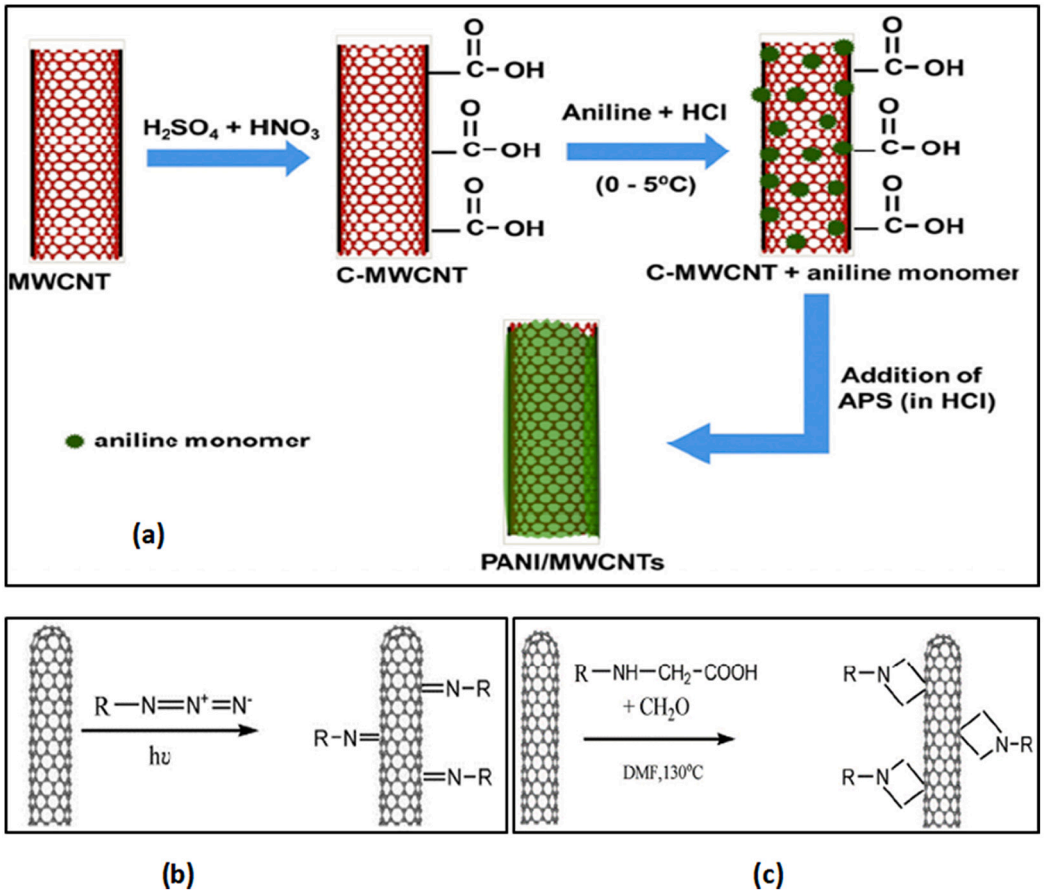

Fig. 7. Covalent functionalization of CNTs through (a) oxidation process (b) photochemical (c) electrochemical [38,41].

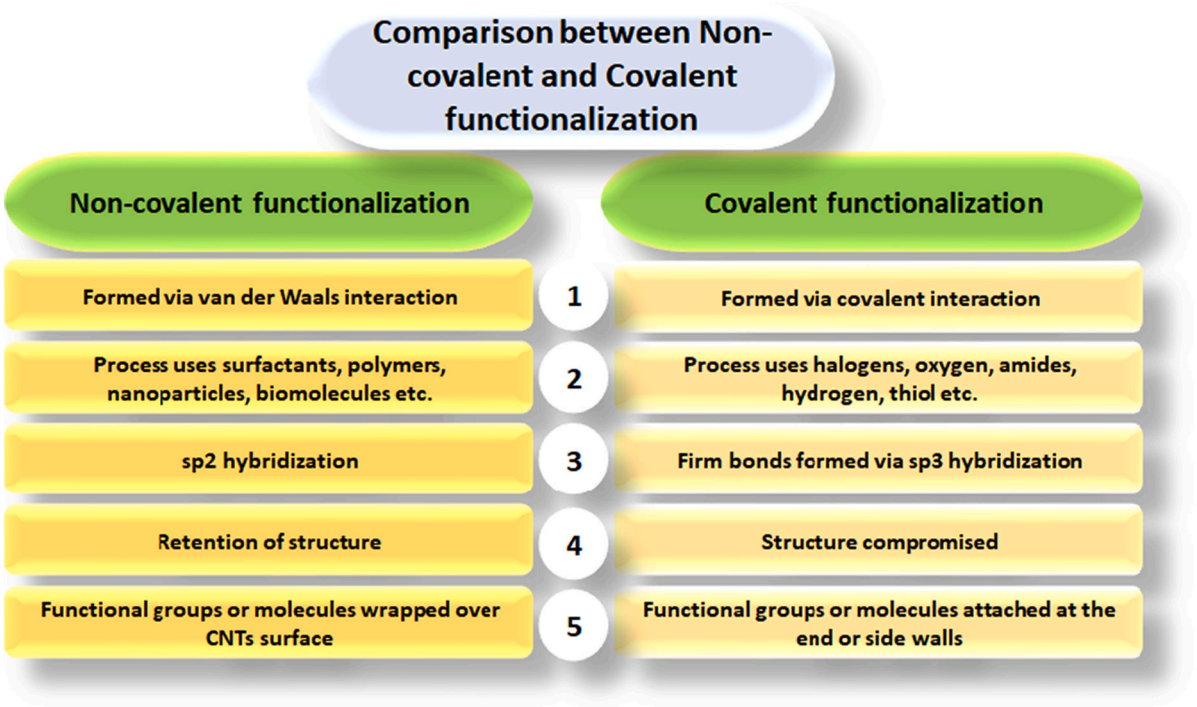

Fig. 8. Typical differences between non-covalent and covalent functionalization.

or polymers are used), CH- π involving interactions of biomolecules and CNTs and through electrostatic interactions. It is well known that poor dispersion of CNTs in common solvents has been a big impediment in the fabrication and usage of biosensors. Presently, non-covalent functionalization using high-affinity species like conjugated aromatics, polymers and surfactants have improved the solubility of CNTs subsequently enhancing adsorption of molecules to their surfaces [15]. For example, the derivative of amine-reactive pyrene [46] and pyrene conjugated glycodendrimers [47] have been used for CNTs functionalization. Fig. 9 (a) displays a pyrene molecule functionalized SWCNTs [48] and Fig. 9 (b) immobilization of proteins on the side-wall of SWCNTs using 1-pyrenebutanoic acid, succinimidyl ester (PBSE) [49]. The anchored PBSE molecule on SWCNTs side-walls was extremely resistant to desorption in an aqueous solution.

A discussion has been presented in the sensing mechanisms of metal phthalocyanine (MPc) noncovalently functionalized metallic CNT (9,0) zigzag and metallic CNT (5,5) armchair for the detection of H_2s and acetone. An examination of the transport and electronic properties and the effect of the central transition metal atoms (Fe, Co, and Mn) has been performed. Results showed that MPc adsorbed onto the surface of CNTs leads to the quantum interference-effect. With the adsorption of H_2S and acetone, an observation of charge re-organization of the device which leads to conductance modulation was noted. This implies that the sensitivity of H_2S and acetone is mainly due to the electron transfer between the devices and the target analytes [50]. Also, a noncovalent functionalization approach was used to fabricate a CNT-based electrochemical sensor (MWCNTs-polyazocarmine B (PACB) nanofilm electrode) for sensing nitric oxide (NO). The result showed an excellent electrocatalytic activity to NO gas with the sensor exhibiting high sensitivity, good stability, reproducibility and selectivity thus being effective in monitoring and detection of NO [51].

4. CNT-based biosensors

Biosensors are devices or probes that integrates elements with unique binding specificities like enzymes, DNA, antibodies, NPs and aptamer towards target analytes [15]. Typically, biosensors are composed of an analyte, the bio-receptor, a transducer and a signal processor (electronics and display) (Fig. 10) [52]. Their working principle involves an interaction of target (analyte) with the recognition molecule to produce a signal in the form of heat, pH, light, mass or charge change, tissue (plant or animal) through biorecognition interaction. Then the biorecognition event is converted into an electrical signal by transducer through a process called signalization.

The signal can be optical, electrical, electrochemical, gravimetrical etc. which corresponds to the number of interactions between analyte and bioreceptor. The transduced signal is thereafter amplified and undergoes digital conversion and channelled to the display which gives readable data in form of graphs, tables, figures or numerical values [53]. For example, the resistance of pristine MWCNT thin film has been used as a sensing parameter in the detection of CO_2 gas. The sensor response (SR) was estimated using the electrical resistance of MWCNT in the air (R_a) and in the presence of CO_2 gas (R_g) as represented by Eq. (1).

$$\%SR = \frac{|R_a - R_g|}{R_a} \times 100 \quad (1)$$

From Fig. 11, a decrease of the energy of pristine MWCNTs on absorbing of reducing gas molecules was observed and attributed to having fewer electrons in the conduction band. Conversely, the energy of pristine MWCNTs increased in the absorbing oxidizing gas molecules as a result of free electrons in the conduction band [54].

Compared to other NMs, CNTs exhibit extraordinary physiochemical properties and excellent strength due to their nano-structural tubular nature hence their promising use in biosensors development. Owing to their outstanding surface to volume ratio and good electron transfer properties, the electronic conductance CNTs is highly influenced by minor surface perturbations like those related to the binding of macromolecules [53]. Additionally, CNTs have superior conductivity (about 100 times better than copper), good chemical stability, great biocompatibility, high selectivity and sensitivity [55]. Their decent optical properties (near infra-red photoluminescence and resonance Raman scattering) are ideal for the detection of biological species [56].

These nanostructured materials can be easily modified by suitable chemicals attached at the side-walls or the end of CNTs to enhance their properties and functionalities. For instance, through the functionalization of pristine CNTs on their surface and converting them to hydrophilic CNTs, they increasingly become biocompatible and biodegradable [57]. In the recent past, voluminous research work and innovations have been done on this field as attested in Fig. 12 where the number of publications for the last 10 years and countries leading in research under the title search 'carbon nanotubes biosensors' have been presented.

The CNTs-based biosensors can be grouped into two; electrochemical biosensors and optical biosensors. The mechanism of the electrochemical biosensors involves three-electrode electrochemical cells namely; the reference electrode, the counter electrode and working electrodes which changes/transfers a biorecognition signal into an electrochemical signal. The Enzyme immobilization on the working electrode is responsible for recognition thus creating a current or

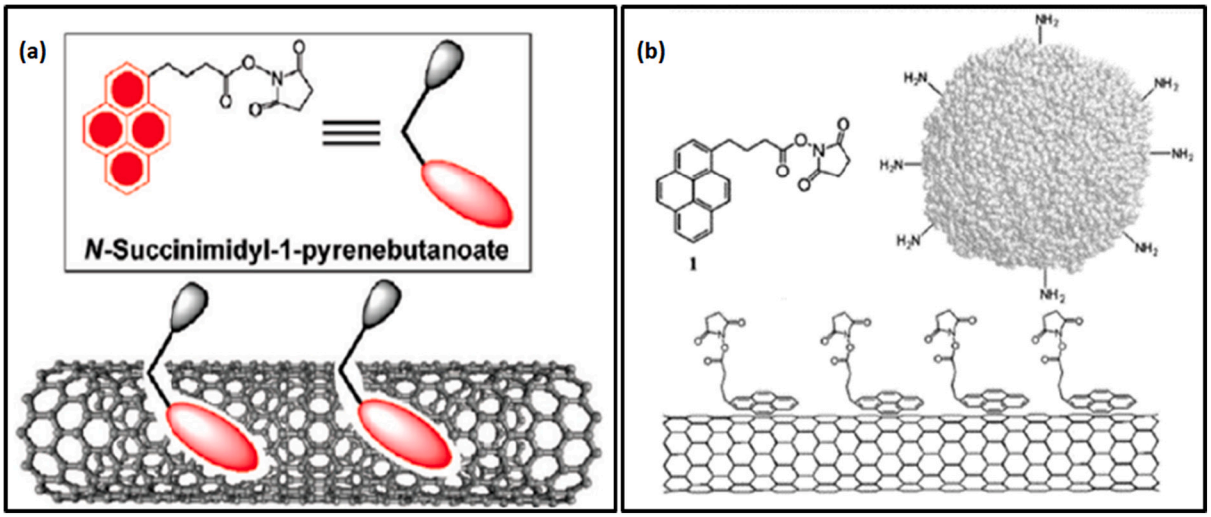

Fig. 9. Functionalization of SWCNTs using Pyrene-based molecule PBSE [48] (b) Immobilization of proteins on SWCNTs using PBSE [49].

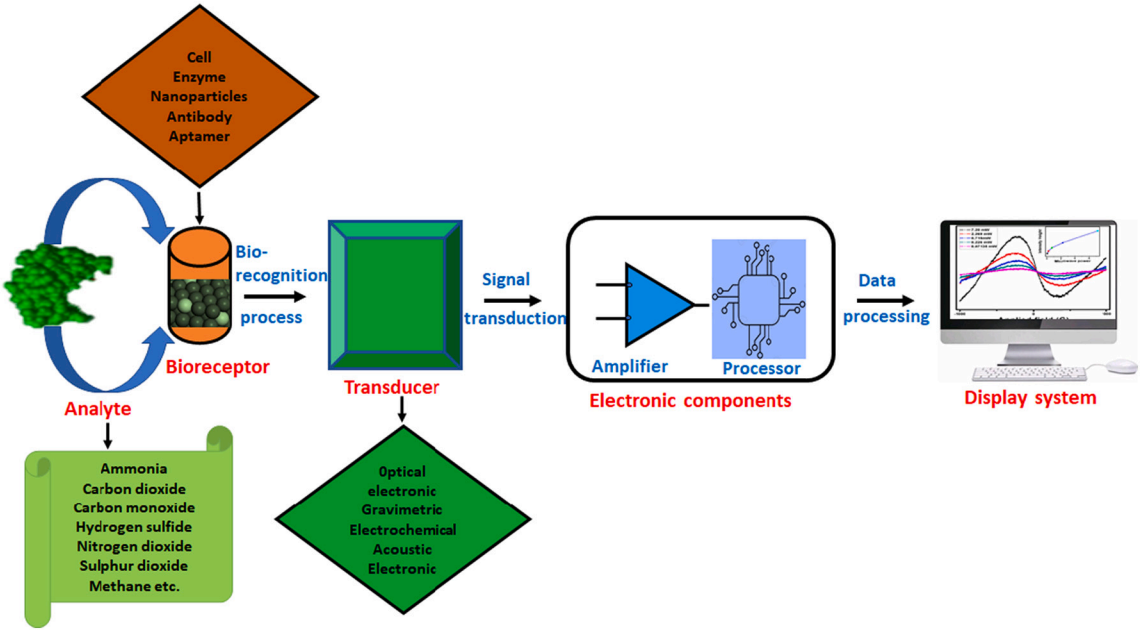

Fig. 10. Sketch of the typical biosensor with its components: analyte, bioreceptor, transducer, electronic components, and display system.

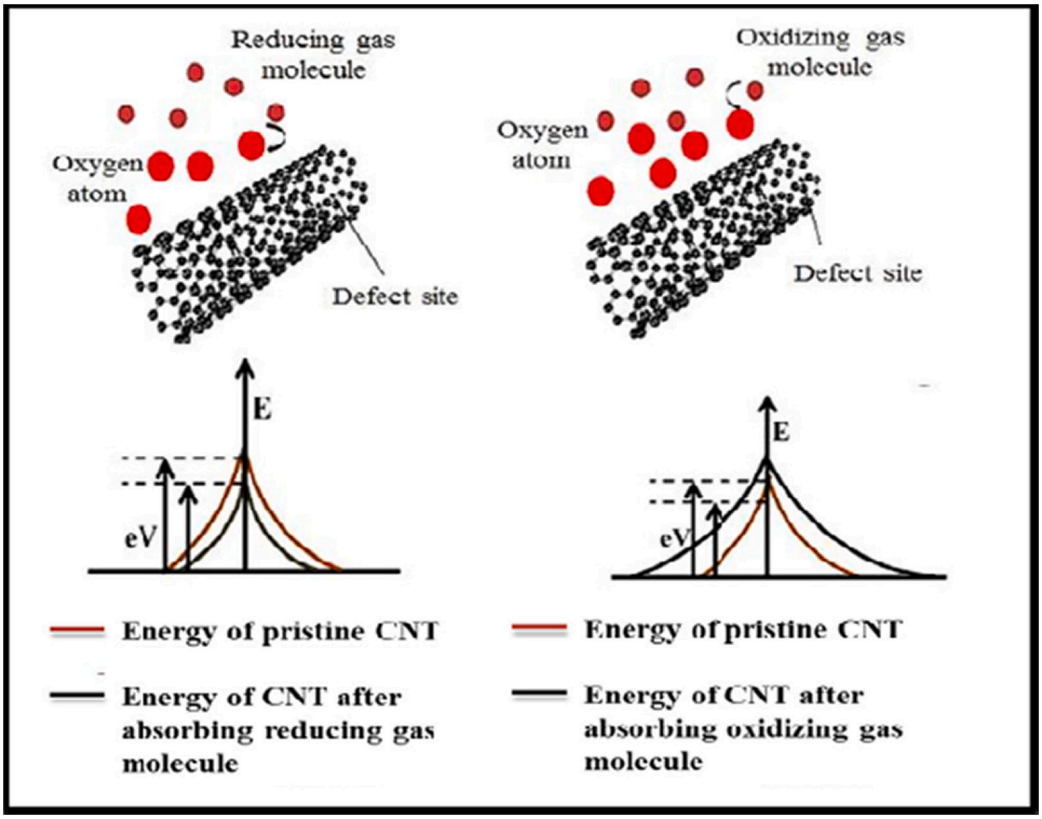

Fig. 11. Mechanisms of pristine MWCNTs sensor for detection of CO_2 gas.

contributing to voltage production [19]. Based on the literature [52], the electrochemical biosensors can further be classified into bio-enzymatic (CNTs-paste enzyme electrode, CNTs-modified electrode with immobilized enzymes and CNTs-forest electrodes with immobilized enzymes) and bio-affinity biosensors (CNTs-DNA-based electrochemical biosensors and CNTs-immunosensors) (Fig. 13).

Conversely, the optical biosensors work on the principle of detecting and measuring the analyte and the target biomolecules interactions via photon measurements [53]. Optical biosensors use antibodies, tissues, enzymes, whole cells and aptamers as biorecognition elements. The transduction process in optical biosensors induces a change in the absorption, reflection, refraction, transmission, amplitude, phase and frequency or polarization in response to chemical or physical changes formed by the recognition elements. Optical biosensors can be grouped

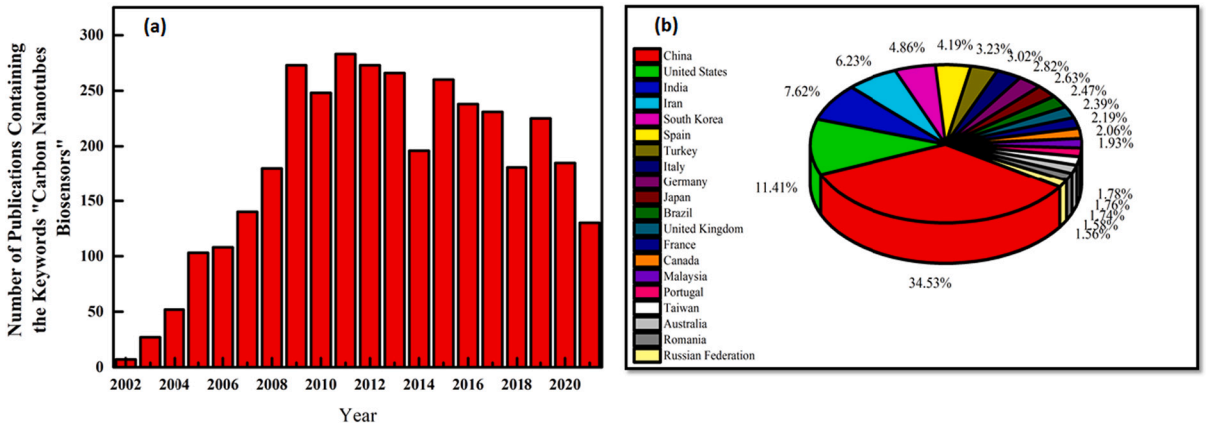

Fig. 12. (a) The number of publications obtained from SCOPUS based on a search title 'carbon nanotubes biosensors' from 2002 to August 5, 2021 (b) The top 20 countries leading in research on CNT-based biosensors.

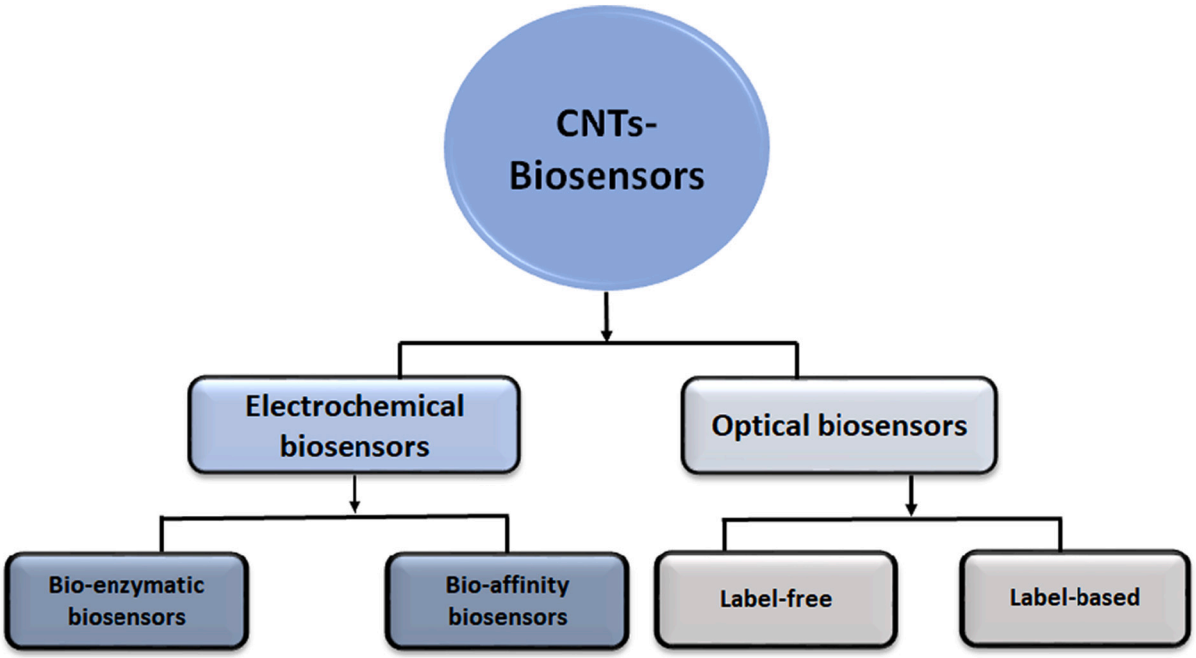

Fig. 13. CNTs-based biosensors.

into two namely; label-free and label-based. In label-free, the interaction of the transducer with the analyte generates the detected signal whereas in label-based sensing the optical signal is produced by fluorescence, luminescent and calorimetric methods [53].

Diagnostic devices and biosensors related to CNTs have been employed for extremely sensitive detection/sensing of analytes in industries, biological sensing, food quality examination, industries and environmental monitoring and detection. For instance, CNTs-based electrochemical sensors have been developed to sense metabolites, biomarkers of proteins and ions [58]. Lin et al. have reported a CNT-glucose biosensor for cholesterol detection. The biosensor consists of modified printed electrodes containing cholesterol esterase, MWCNTs, oxidase and peroxidase resulting in a very sensitive way of measuring cholesterol in blood [59]. Similarly, RNA aptasensor has been developed by coating SWCNTs using RNA aptamers of protein on an alumina electrode to detect glycoproteins-related diseases in blood [60]. Nitric oxide has been selectively detected by using single-stranded d(AT)15 DNA oligonucleotide after being adsorbed and wrapped around SWCNTs [61]. Also, SWCNTs-based biosensor has been developed to detect hydrogen peroxide (H_2O_2) from individual human epidermal carcinoma cells [62].

5. CNT-based biosensors for the detention of gases

The performance of the biosensor is outstanding due to their astonishing linear nature, selective nature, sensitive nature, stable tendencies in addition to their exceptional response time, and reproducibility tendencies when compared with the traditional sensors [63]. The gas adsorption mechanisms of CNT-based sensors are now well known and it has aided to locate available adsorption sites and also provides explanations on the decreasing or increasing of conductivity during CNT-based sensor experiments of gas adsorption [64]. It is evident that there are four main gas adsorption sites in CNTs namely; (1) internal site or interior pore of a tube (2) interstitial or channel site between three adjacent bundles, (3) grooves formed with adjacent tubes and (4) external surface of the tube/bundle as shown in Fig. 14A. In as much as there are many adsorption sites available in CNTs, the properties of gas molecules uniquely dictate their adsorption sites. For example, sulfur

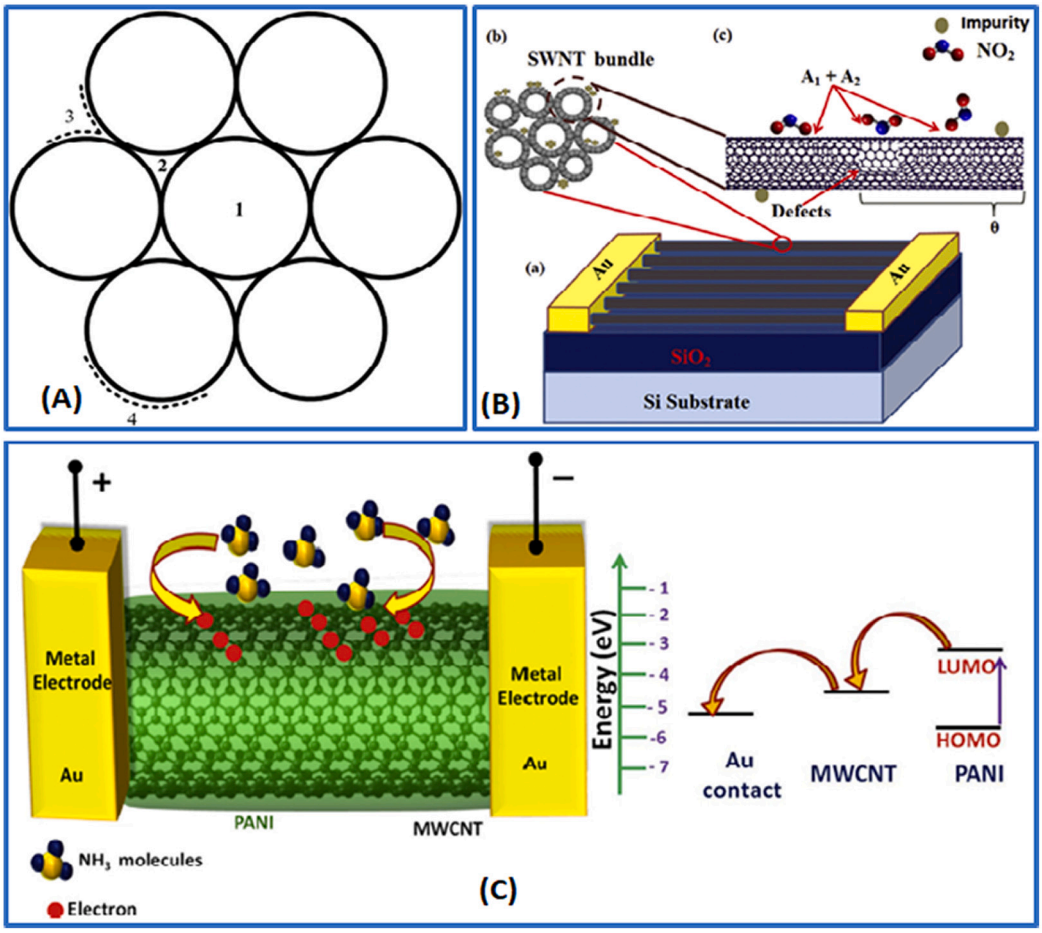

Fig. 14. (A) CNTs adsorption sites (B) Gas sensing mechanism of the SWCNT-based biosensor depicting the chemisorption of the analyte particles (C) Gas sensing mechanism together with the binding energy chart displaying the adsorption of ammonia gas resulting in the corresponding transfer of charge [38,65,66].

hexafluoride gas could be adsorbed at internal and external sites of SWCNTs [65]. Importantly, each adsorption site has designated adsorption energy which is expressed as;

$$E_{ad} = E_{CNT/molecule} - E_{CNT} - E_{molecule} \quad (2)$$

For H_2 gas, the adsorption energy for various are E_{ad}(channels) $>E_{ad}$(grooves) $>E_{ad}$(internal) $>E_{ad}$(surfaces) [65].

After the realization of adsorption sites, mechanisms of gas sensing of CNT-based biosensors ought to be known. The two utmost gas sensing mechanisms regarding chemisorption and physisorption are shown in Fig. 14 **(B and C)** [38,66].

In chemisorption, both reversible and irreversible reaction concurrently occurs on the detecting surface. The two types of reactions encompass the diverse adsorption rate having different accessible locations with equivalent activation energy. The sensing rate in physisorption is quicker during the early phase when the gases are presented but gradually gets sluggish with additional exposure to the gases. This could be as a result of the saturation in the reversible locations in the advanced section of the reaction, which is not the same from the early phase when both the reversible and irreversible locations are conveyed in the response of the biosensor [67].

The wide-ranging tendencies of SWCNTs in terms of their conductive potentialities (having both conducting and semi-conducting nanotubes) makes the AE fluctuate in the adsorption location. Also, it has been demonstrated from the analysis of TEM as well as Raman spectroscopy that definite impurities existing on the walls of CNTs similarly convey in the adsorption locations for chemisorption. As also seen in Fig. 14 **C**, the modification in the binding energy illustrated in the band chart in physisorption ensues due to the transfer of electrons among the nanocomposite-based sensing location and the quantified gases [68,69]. In this instance, an integrated influence of the chemisorption and physisorption ensues during the gas particles exposure. The reaction between the gas particles and nanocomposite-based MWCNTs occur based on an ion-dipole interface. The coplanar tendency of the PANI composites in this instance cause stress-free electrons to transfer from the quantified gas (NH_3 gases).

This steered to the localization of polarons that was a result of the net transfer of charges among the NC and particles of the gases. The localization successively results in the modification in the resistance. An additional reason for the modification in the resultant resistance could be accredited to the decline of the connectivity of the nanocomposite owing to the adsorption of the particles of the gases. The loosening between the nanocomposite makes it stress-free for desorption of the particles of the gases without the effort of exterior energy. Although both the chemisorption and physisorption occur concurrently, physisorption is predominant than others, consequently assisting in its swift response and recovery durations [67].

Albeit, some of the momentous existing research activities undertaken on the gas sensing of diverse gases using CNTs-based biosensors are highlighted below and their summary is provided in Table 3. Hydrogen peroxide (H_2O_2) gas sensing study using MWCNT-based biosensor (Co_3O_4/MWCNTs/gelatin composite) has been reported [70]. The MWCNTs used were of length 10–30 μm and outer diameter of less than 8 nm. A 0.5 wt% of Nafion diluted in a mixture of ethanol-water was used to prepare 0.5 wt% of Nafion solution. The Co_3O_4 nanoparticle and MWCNTs were dissolved in 1 mg ml^{-1} aqueous

Table 3
CNTs-based sensors for detection of some gases, indicating the sensor material (SM), limit of detection (LoD), Concentration range (CR) and the Response time (RT) drawn from existing research publications.

SM	Analyte	LoD (ppm)	CR (ppm)	RT (seconds)	References
Polythiophene/SWCNTNs/SiO_2	NO_2	0.01	0.01–10.00	20.00	[76]
SWCNTs/Au nanoparticles (NPs)	NO_2	40.00	40.00–100.00	13.00	[77]
SWCNTs/Pt	NO_2	1.00	1.00–3.00	282.00–294.00	[78]
MWCNTs/Au/Pt	NO_2	0.10	0.10–10.00	120.00–180.00	[79]
SWCNTs/ Hydroxy propyl cellulose	NO_2	0.03	0.30–0.03	300.00	[80]
SWCNTs/ Polytetrafluoroethylene/Silicon	NO_2	0.75	0.75–5.00	240.00	[81]
SWCNTs/ SiO_2/Au	H_2S	0.003	0.02–1.00	360.00–480.00	[82]
SWCNTs/SiO_2	H_2S	5.00	5.00–200.00	900.00	[83]
SWCNTs/Cu	H_2S	5.00	5.00–200.00	7.00	[84]
MWCNTs/Cu	H_2S	10.00	10.00–100.00	70.00	[85]
CNTs/Glassy carbon electrode	H_2S	0.009	0.009–10.00	1800.00	[86]
MWCNTs-COOH	H_2S	0.31	0.31–10.00	363.60	[74]
MWCNTs/PANI/Au	H_2O_2	0.30	3.00–300.00	2.00–12.00	[87]
MWCNTs/Au/Ag	H_2O_2	0.017	0.0017–0.57	5.00	[88]
MWCNTs/Chitosan	H_2O_2	170.00	170.00–3400.00	5.00	[89]
MWCNTs/Prussian blue	H_2O_2	0.65	17.00–102.00	4.00	[90]
MWCNTs/$C_{11}H_{10}FeO_2$/bovine serum albumin	H_2O_2	0.0005	0.0005–0.003	20.00	[91]
CNTs/PDDA/PSS	NH_3	5.00	5.00–25.00	20.00	[92]
SWCNs/Cu	NH_3	100	100.824.00	10.00	[93]
MWCNTs/Co	NH_3	14	14.00–800.00	30–50	[94]
SWCNTs/PMMA	NH_3	1.00	1.00–500.00	600.00	[95]
MWCNTTs/ Ag/Au/Cr	NH_3	10.00	10.00–100.00	30.00	[96]
MWCNTs/Pd	NH_3	5.00	5.00–100.00	10.00–15.00	[97]
MWCNTs/PCz	NH_3	0.89	0.89–311.00	7	[98]
CNTs/Au	NH_3	40.00	40.00–200.00	37.50–39.78	[99]
SWCNTs/Pd	NH_3	0.73	1.00–50.00	88.20	[100]
MWCNTs/Pt	NH_3	5.00	5.00–10,000.00	40.00–130.00	[101]
MWCNTs/Pd	NH_3	100.00	100.00–500.00	30.00	[102]
SWCNTs/Pd	NH_3	40.00	40.00–400.00	5.00–10.00	[103]
CNTs/PAA/Amino	CO_2	75.00	1000.00–4000.00	184.20	[73]
CNTs/Si/Au	CO_2	50	50–800	250	[104]
CNTs/Pt/Ru/Ag	CO_2	0.1	0.1–10,000	120–180	[105]
SWCNTs/Pd	CO_2	100.00	100.00–10,000.00	3.00	[106]
SWCNTs/SnO2	CO_2	100.00	100.00–10,000.00	1000.00	[107]
[$CpCo_{I2}$]-SWCNTs	CO	50.00	800.00–3000.00	60.00	[108]
MWCNTs/Rh	CO	2	2–20	600	[109]
MWCNTs/ Co3O4/PEI	CO	5.00	5.00–1000.00	4.70	[110]
MWCNTs/Pt	CO	200.00	200.00–800.00	13.54–18.55	[111]
SWCNTs/SnO_2	CO	1.00	1.00–100.00	2.00	[112]
MWCNTs/Co/SiO_2	CH_4	100.00	100.00–150.00	215.00	[113]
MWCNTs/SnO2	CH_4	0.01	0.01–10.00	600.00	[114]
MWCNTs/ZnO/SiO2	CH_4	2.00	2.00–10.00	0.022	[115]
SWCNTs/Pt	CH_4	50.00	50.00–200.00	180.00	[116]
MWCNTs/Ag	CH_4	15.00	40.00–100.00	10.00	[117]
CNTs/SiO_2/Au	C_2H_5OH	50.00	50.00–800.00	400.00	[118]
MWCNTs/PEG	C_2H_5OH	9.00	10.00–100.00	55.00–65.00	[119]
MWCNTs/Alumina	C_2H_5OH	0.50	50.00–500.00	95.00–225.00	[120]
MWCNs/Cr2O3	C_2H_5OH	10.00	10.00–800.00	8.00	[121]
SWCNTs/In_2O_3	C_2H_5OH	1.00	1.00–9.00	60.00	[122]
F_{16}CoPc/MWCNTs-COOH	Cl	0.50	40.00–2000.00	–	[123]
F_{16}CuPc/SWCNTs-COOH	Cl	0.27	0.10–2.00	9.00–240.00	[97]
F_{16}ZnPc/MWCNTs-COOH	Cl	0.06	0.102	14.00	[98]

solution and ultra-sonification for 2 h to ensure a black and homogeneous dispersion of 2 mg ml^{-1} MWCNTs and 2 mg ml^{-1} of Co_2O_4 mg ml^{-1} NPs was realized. The biosensor (Co_3O_4/MWCNTs/gelatin/HRP/Nafion/GCE) was fabricated founded on the immobilization of horseradish peroxide (HRP) through cross-linking on glassy carbon electrode modified with Co_3O_4 NPs, MWCNTs and gelatin as shown in Fig. 15a. Primarily, it was realized that MWCNTs and Co_3O_4 NPs increased the surface area of the electrode for immobilization of enzyme and enabled the rate of electron transfer. At pH of 7.0, the biosensor exhibited a response of 5 s. The linear response range and detection limit of the optimized biosensor were 7.4×10^{-7} to 1.9×10^{-5} M (correlation coefficient of 0.9972 Fig. 15b and 7.4×10^{-7} respectively. During H_2O_2 gas testing, the average recovery was measured to be 100.78± 0.89 [70].

A biosensor produced from metal-organic frameworks-MOFs (ZIF-67 (Co)/MWCNT) composite was used for the detection of H_2O_2. The glassy carbon electrode (GCE) of length 3 mm was polished using alumina slurry then followed by washing by deionized water and sonicated before drying. The 0.02 wt% was used to disperse 1 mg mL^{-1} of MWCNTs. Later, MWCNTs solution and 1 mg mL^{-1} ZIF-67 (Co) suspension were mixed in the ration 1:1 and HRP aqueous solution was added and mixed. Finally, the 0.1 mg mL^{-1} of HRP, MWCNTs and ZIF-67 (Co) mixture (6 μL) was coated onto the GCE surface then dried at a temperature of 4 °C. The biosensor (ZIF-67(Co)/MWCNT/HRP/GCE) showed exceptional performance because of the ZIF-67(Co) integrating well with MWCNTs and HRP. It is important to note that MOFs has good catalytic properties so their combination with immobilized enzymes only reinforces catalysis. Again, it was observed that the good conductivity properties of MWCNTs enhanced electron transport between the electrode and immobilized enzyme and offered a hydrophilic/hydrophobic balanced environment conducive for enzymes. The reported sensitivity of this biosensor of 315 μA mM to 1 cm^{-2} (Fig. 15 c) was higher when compared to previous MOFs-HRP biosensors [71].

Fig. 16 shows a sketch of NO sensor formed using a non-covalent approach of MWCNTs and azocarmine B (ACB). The ACB is

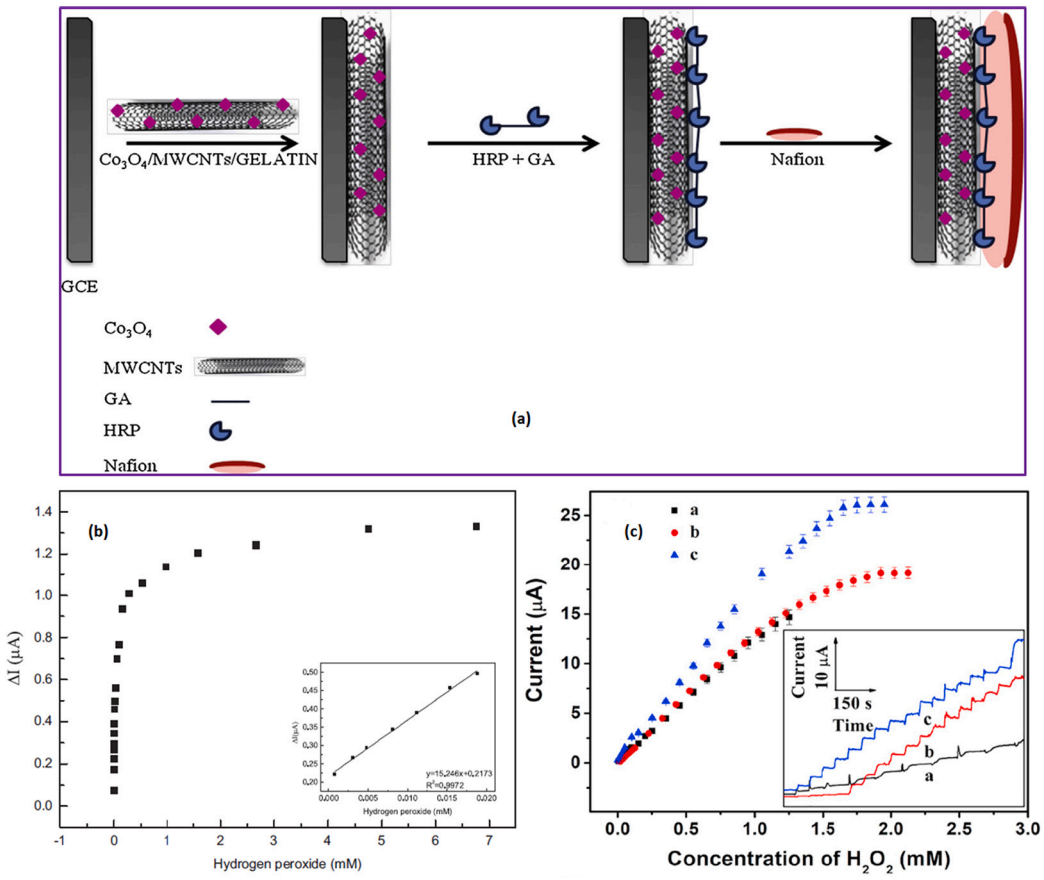

Fig. 15. (a) Electrode modification (b) Co_3O_4/MWCNTs/gelatin/HRP/Nafion/GCE-biosensor's amperometric response at −0.30 V (c) ZIF-67(Co)/MWCNTs-biosensor curves [70,71].

fundamentally used to facilitate MWCNT solubility in water. For the preparation of the sensor, a slurry of alumina was used to polish GCE of a diameter of 3.0 mm and washed in HNO3 in the ratio of 1:1, it was washed and sonicated in HNO_3, ethanol and water. Then followed the casting of MWCNTs-ACB (4μL 1 mg mL^{-1}) onto GSE and drying with an infra-red lamp. By sweeping from −0.6 V to 1.5 V, the electro-polymerization of ABC was done at a rate of 100 mV s-1 in an H_2SO_4 solution of 0.5 mol L^{-1} containing 5 mg mL^{-1} ABC. Finally, casting off 2 μL 1% Nafion solution on MWCNTs-ACB/PACB/GCE to produce an electrode sensor for amperometric detection of NO in liver cells of a rat. The measurement showed brilliant electrocatalytic activity to oxidation of NO. A linear increase of oxidation current with NO concentration was observed in the range 2.2×10^{-7} to 1.2×10^{-4} mol L^{-1} with 2.8×10^{-8} mol L^{-1} as a low detection limit [51].

Also, Santhosh et al. have reported a fabrication of an amperometric sensor (MWNT-g-PDPA-ME) devised to detect CO. To demonstrate the electroactivity of this sensor, cyclic voltammetry was employed to develop a modified electrode. It was established that the sensor had a high sensitivity for oxidation of CO in 0.5 M $HClO_4$. With correlation coefficient $r = 0.9941$, a good linear concentration range of 10 to 200 ppm was obtained. Also, a quick response i.e., 96% and 98% for 2 and 3 s recovery times to 100 ppm of CO were determined [72]. Equally, Shivananju et al. [73] have fabricated a sensor for sensing CO_2 at room temperature using Fiber Bragg Grating (FBG) which is clad-etched and polyallylamine (PAA)-amino-CNTs. The sensor's working principle is based on the change in the refractive index of the fiber after the interaction of CO_2 gas molecules with PAA-amino-CNTs resulting in the shift in Bragg wavelength. The sensor was designed to detect CO_2 gas in the range of 1000 to 4000 ppm with a limit of detection found of 75 ppm.

In this study [54] MWCNTs were synthesized through a direct liquid injection chemical vapor deposition (DLICVD) method from ethanol using Co NPs at a temperature of 750 °C. The Co NPs was prepared via the sol-gel method and exhibited a pure composition for efficient catalytic activity for the synthesis of MWCNT. The grown MWCNTs were purified and functionalized using nitic acid and sulphuric acid in the ratio 3:1. The fabricated sensor produced maximum sensitivity of 2.1 at 500 ppm with recovery time and fast response of 49.62 s and 30.21 s for CO_2 gas respectively. Large surface area and conducting channels were factors attributed to the improved detection.

In this study [74], a hydrogen sulfide gas sensor is reported. The electrodes of the sensor (working and counter) were assembled using carboxylated-MWCNTs (MWCNTs-COOH). The polytetrafluoroethylene (PTFE) was used as hydrophilic membrane and the field emission scanning electron microscope (FESEM) measurements show that the MWCNTs-COOH was fairly distributed in the membrane. EDX data revealed 85.95 wt% and 12.95 wt% of carbon and oxygen on the working electrode respectively. Through cyclic voltammetry, the sensor response to H_2S was revealed and the chronoamperometry measured the response as 56 ppm. The linear behaviour was up to 16 ppm and detection limit of 310 ppm with a sensitivity of 48 h. Recovery time and average response of 4.13 and 6.06 min respectively was also found.

MWCNTs whose length is in the range 1–2 μm and diameter of 20–40 nm produced through CVD were treated using H_2SO_4/HNO_3 to remove extra carbonaceous materials and improve dispersion. Sonication and stirring took 30 mins each and the mixture was washed using in water until neutral pH was achieved. An in-situ polymerization technique was used to produce PANI/MWCNT nanocomposites using C-MWCNTs composite, aniline and HCl as raw materials. Structural characterization of PANI/MWCNTs nanocomposite was done using UV–Vis, X-ray, XPS, HRTEM and FTIR. The nanocomposite-based gas sensors (C-MWCNTs

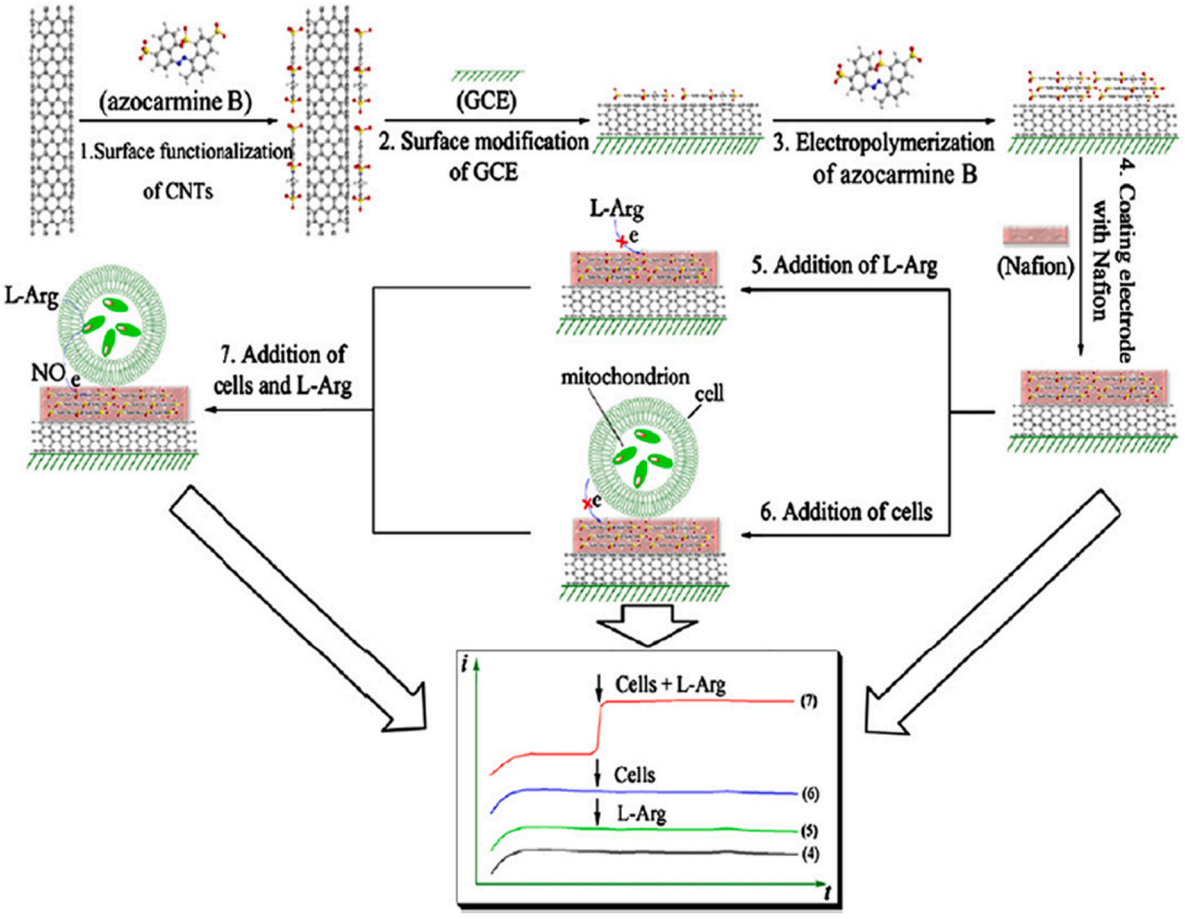

Fig. 16. Assembly of MWCNTs-ACB/PACB/GCE biosensor to detect NO in rat liver.

and PANI/MWCNTs) showed impressive NH_3 sensing characteristics. PANI/MWCNTs showed superior sensor performance in 2–10 ppm concentration due to the presence of polyaniline functional group on MWCNT surface. Equally excellent reversibility and fast response exhibited by his sensor were ascribed to improved charge transfer via the C-MWCNT thick layer. Fig. 17 shows the selectivity and effect of O_2 on NH_3 response. The selectivity of 15% for 2 ppm of NH_3 and complete recovery of the sensor under nitrogen was shown. The study registers PANI/MWCNTs as less expensive and room temperature sensors for NH_3 gas sensing [38].

The SWCNTs sample was dispersed in a solution containing sodium hydroxide, water and sodium lauryl sulphate to produce pristine SWCNTs. Indium Tin Oxide (5 wt%) NPs of diameter < 50 nm and purity of 99.99%, was used to functionalize pristine SWCNTs. The mixture of CNT + ITO Nps went through sonication for 1 h and was deposited on a flexible plastic substrate. At the sample sides, two strips of silver paste were deposited and the system was used as a sensor. The sensor showed increased sensitivity with a detection limit of 13 ppb for NH_3 concentration above 200 ppb. The introduction of ITO NPs led to a three-fold increase in sensitivity when compared to pristine SWCNTs [75].

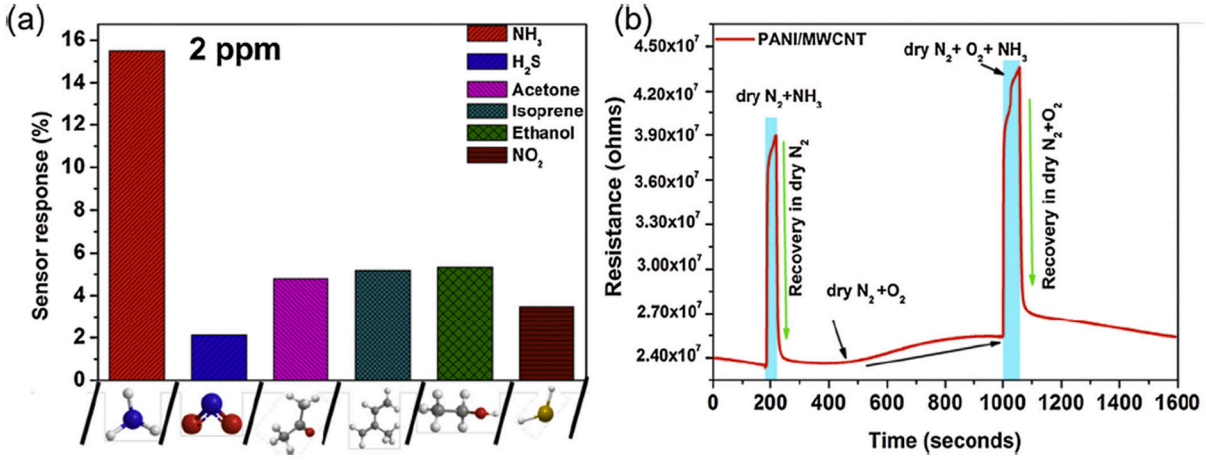

Fig. 17. (a) PANI/MWCNT selectivity (b) Effect of O_2 on NH_3 detection properties of PANI/MWCNT [38].

6. Limitations and future perspectives of gas detection using CNT-based biosensor

In the present situation, although a considerable amount of research studies has been undertaken on CNT-based biosensors for the detention of gases, there are still ambiguities in the form of challenges that needs to be solved. Some of the basic challenges include costly synthesis procedures as well as the high heat energy required especially for MWCNTs. Also, the toxicity of CNTs has a negative influence on creatures owing to their ecological discharge and lesser lifeline when compared to silicon garbage dumps. Furthermore, owing to the extremely sensitive nature of CNTs, the influence of humidity and temperature on the CNTs-based biosensors are exceptionally high, and this could result in a high error of probability in the course of precise measurements [10].

As stated by [124] other observed limitations that are allied with CNTs-based gas sensing are the lesser conductivity nature of MWCNTs at normal temperature, discrepancies in the response of the biosensors due to the distance between the cathode and anode at precise voltages.

According to [125] some CNT-based biosensors have truncated discharge energy along with reduced charge transfer rate and diffusion kinetics. This decreases the response time of the biosensors towards the gas particles, particularly for biosensors that are functioning on several gases. Also, as reported by [126] in few circumstances the transfer of charge hardly occurs efficiently between the CNTs and the quantified gas. This generates a feeble bond between them, which consequently affects the limit of detection for such CNTs-based biosensors.

Another issue with some of the gas sensing is the oxidation of the quantified gas when it is presented in the chamber in a truncated concentration [127]. Also, the oxidation issue is instigated by the occurrence of metallic NPs along with the CNTs. This reduces the efficiency of the CNTs to sense the gas at a truncated concentration. The rate of recovery of most of the CNT-based gas sensing is another issue, which brings down the potential of these gas sensing to be utilized for an elongated period and real-time benefits. Most of such GS displayed truncated sensitivities towards the analytes and this influences their adsorption energy (AE), selective and reversible tendencies as well as response time [128]. Also, the amount of gas particles that can be sensed with a CN-based GS are restricted to the ones having high binding energy and transfer of charge [7].

Similarly, the sensitive tendencies of such gas sensing are also restricted by the binding energy of the particles they bind with the partitions of the CNTs. Also, the percentage of inert gases that could be detected by some of the CNT-based gas sensings is restricted owing to the higher possibility of the sensing of gas particles with truncated activation time. The slow response time and recovery times of some of these gas sensing are other problems that require attention [67].

In summary, some of the other challenges as per the synthesis and applications of the present existing CNT-based gas sensing as adopted from the review studies of [31,67] are:

- Most of the existing CNT-based gas sensing have a truncated selective tendency towards precise gases.
- The difficulties in fabrication such as the expensive and intricate fabrication procedure, difficulties in sustaining the same physiognomies of the invented prototypes, etc.
- The difficulties in the reutilization in the responses.
- The heterogeneous tendencies of the lengths and deficiencies of the nanotubes give ensemble-mean possessions.
- The concentrations of the different measured gases by a sole CNT-based gas sensing are not reliable.
- The huge deficiency densities in MWCNTs are due to the absence of heat energy.
- The detection ability of most of the CNT-based gas sensing is restricted to particles comprising of substantial binding energies.
- The gaseous stage sanitization of (CVD) synthesis comprises of metallic contaminations as well as truncated-yield production.

With all these existing identified challenges of which some are already been mitigated. However, there can still be a way out for other limitations that are yet to be addressed via the following suggestions:

Continue prospects on the synthesis process of CNTs and fabrication of CNTs-based gas sensing: Although much has been done in this regard. However, one of the promising solutions concerning the synthesis process of CNTs is by employing other methods like arc discharge and laser ablation procedures. For the CVD procedure, the cleansing of synthesized CNTs is dependent on the substrates and catalysts employed for producing them. The influence of environmental features such as temperature, humidity, etc. can be refuted by their combination with other semiconducting and conducting constituents to form discerning constituents on the detecting part of the gas sensing. The harmfulness of the gas sensing could be reduced by using the gas sensing in an inert scenario such as Argon. The extent of the decrease of the semiconducting CNTs and the upsurge of the metallic CNTs could be carried out by advancing the cleansing and arranging phase after their production. According to [129], the issue associated with the interaction of gases for the period of testing in real-time processes could be overcome through the dynamic threshold where the extent of the response connected with a specific gas could be categorised to diminish the erroneous output in the monitoring section. Also, the functionalization undertaken on CNT-based gas sensing could be improved to target precise gases around the physiochemical possessions. This can be done by inducing the selective tendencies on the sensing part of the models. Hence, acting on a precise gas. The gas sensing should as well be enhanced to be operated at room temperature, instead of higher temperatures. This will in no doubt enhance the potential application of gas sensing, facilitating safer sensing of hazardous gases [10].

As suggested by [130], the lasting stability of the gas sensing vis-à-vis their sensitive tendencies should be improved through surface modification of the detecting part of the CNT-based GS. The stiffness and durability of some of the existing GS can be evolved by varying the fabrication procedure. Printing machineries with elastic substrates is a positive choice that could be chosen for longer periods. The utilization of CNT-based ionization gas sensing would be employed to sense gases with lesser power consumption and interrupted voltages. Gas sensing would function in an extensive degree of concentrations, having quicker response time and recovery time.

According to [67], the market assessment for the production and application of CN-based gas sensing indicates an exponential increase from about 4.6 billion dollars in the year 2018 to an anticipated value of about 10 billion dollars in the year 2023.

The request for lightweight constituents as electronics materials for technological advancement is relatively high for a wide-ranging of applications in several aspects such as the aerospace and defence sectors as well as nano materials. These lightweight constituents are also being used for evolving polymers, biomedical, chemical, energy and optical devices. Among the various categories of CNTs, MWCNTs are anticipated to have advanced fabrication and applications owing to their advanced compatibility for creating translucent electrodes, conductive heating films, shifts and chemicals biosensor as well as their applications in thermal and solar industries [67].

7. Conclusion and recommendations

It is apparent that the noxious gases are a public health problem and climate change influencers. Mitigation in the form of gas sensing through biosensors appears promising strategy as attested by reviewed studies centred basically on the assessment of CNTs-based biosensors for gas sensing. Brief background on CNTs as well as the synthesis and functionalization of CNTs are highlighted. Remarkable achievements in terms of fabrication and detection of the gases via CNTs-based biosensors have also been enumerated. From the reviewed publications, it observed that notwithstanding the achievements made on the applications of CNTs-based biosensors for gas sensing, there are still some

limitations in the form of defects in some of the existing studies that require further investigation to mitigate and remedy both at the starting and application levels. Also emphasised in this study is the possibilities of utilizing of CNTs in combination with other conductive constituents, where such utilization of the resulting syntheses would rise their functional and sustainable tendencies.

Globally, the production capacity of CNTs presently go above numerous thousand tons annually; to be specific (CNT-based gas sensing as regard this present review), is presently heading to a commercialized level. It is therefore concluded, that as a result of the excellent electrical, thermal and mechanical benefits of CNT-based biosensors for gas sensing, the engagement of a variety of CNTs-based biosensors for detecting purposes in the form of gas sensing could result in a considerable transformation in the nanotechnology domain vis-à-vis the fabrication cost, magnitude and the required energy of the biosensors.

It is therefore anticipated that this review study will pave way for the developments that can advance the adoption of new-fangled gas sensory procedures in the form of future prospects of gas detection using CNT-based biosensors that would safeguard and improve the ecosystem as well as the safety and health of humanity.

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Declaration of Competing Interest

There is no conflict whatsoever to declare.

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