

# Recent advances in electrochemical biosensor and gas sensors based on graphene and carbon nanotubes (CNT) - A review

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## Abstract

Graphene and carbon nanotubes (CNTs) based sensors have been extensively studied because of their applications in the detection of various chemicals and biomolecules. From an application point of view, high sensitivity and selectivity is a promising tool for fast detection of gas leakage and early diagnosis of diseases for health care. In the present review article, we provide a comprehensive overview on the recent advances in the development of graphene and CNT based electrochemical biosensors and gas sensors. From the future point of view, special attention is paid to the synthesis techniques for high-performance biosensors and gas sensors. This article focuses on detecting mechanism for various volatile organic compounds (VOCs) gas sensing behavior of the graphene and CNT based sensors. A comparative study of the sensing behavior of pure metal oxide nanoparticles as well as their hybrids with graphene and CNTs has been reported. Copyright © 2017 VBRI Press.

**Keywords:** Graphene, carbon nanotubes (CNT), electrochemical biosensor, gas sensor.

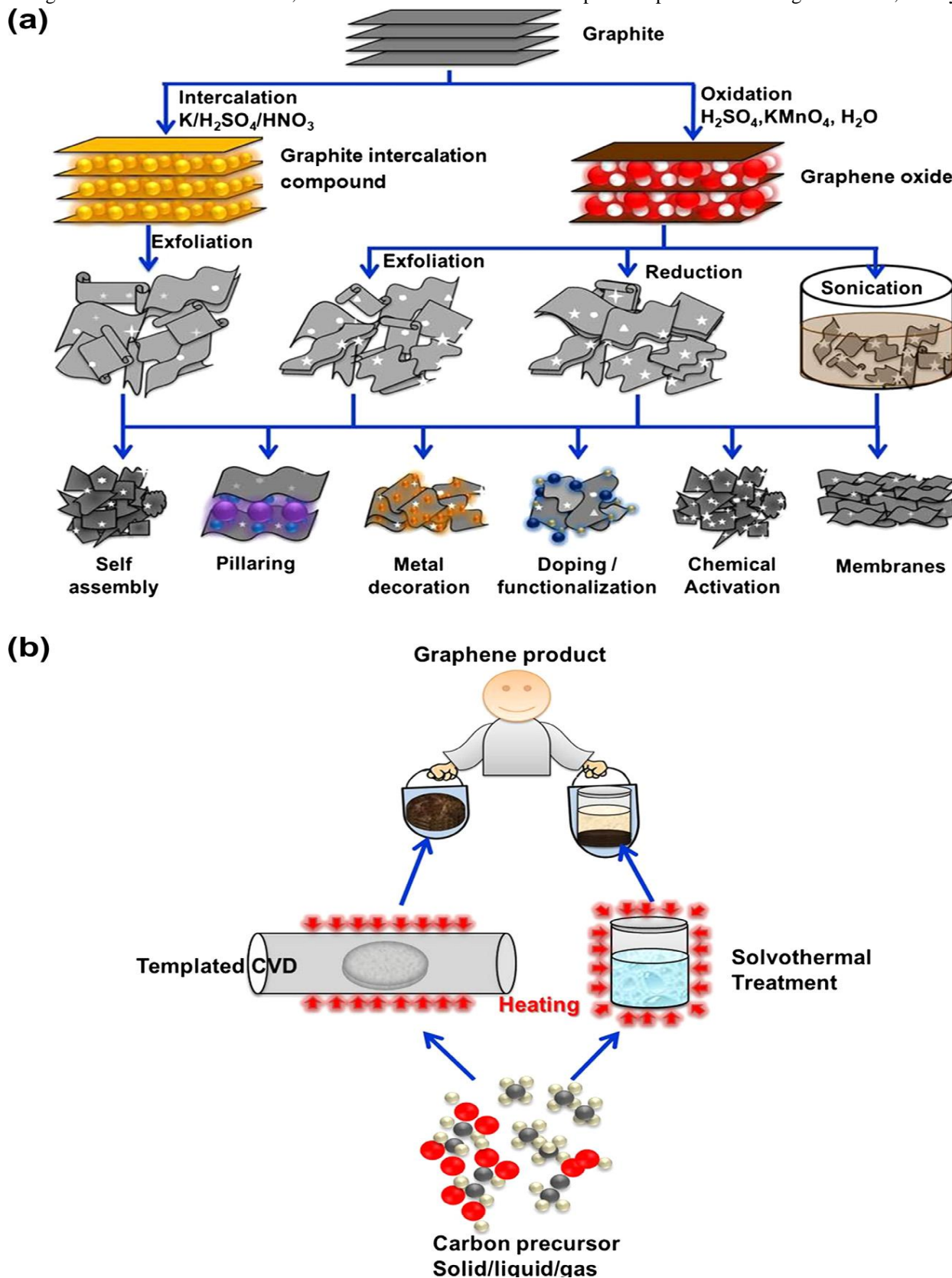
## Introduction

For the past few decades, the vast advancement in the field of sensing technology based on semiconductor metal oxides has attracted the attention of many researchers to provide safety and security to mankind. Air pollution may come from the introduction of other materials into earth's atmosphere either by natural or a man-made source. Air pollution influences human health and cause diseases like mortality, cardiovascular diseases, lung disease and cancer which result in human death as well as damage to other living organisms such as animals and agricultural food crops [1]. Air pollutants are classified as primary and secondary. Primary air pollutants are usually produced by man-made sources. It includes carbon monoxide (CO), sulfur dioxide (SO<sub>x</sub>), nitrogen oxide (NO<sub>x</sub>) and volatile organic compounds (VOCs), whereas secondary pollutants are not emitted directly. They form in the air when primary pollutants react or interact. The best example of secondary air pollutant

is ground level ozone. The major sources of man-made VOCs contributing to pollution are fossil fuels, benzene, methylene chloride, perchloroethylene, toluene, methyl tert-butyl ether (MTBE) and ethylbenzene, formaldehyde. Among VOCs, benzene is one of the most frequently used substance to make other chemicals and industrial manufacturing productions such as plastics, rubber, resins, lubricants, dye, drugs, synthetic fibers, pesticides etc [2, 3] while emission of formaldehyde affects relative humidity within an indoor environment [1]. According to the UK Health Protection Agency (HPA), the occupational standard for 8 hrs toluene exposure is 50 ppm (191 mg/m<sup>3</sup>) [4]. According to GENEVA report, air pollution in 2012 caused the death of around 7 million people worldwide [5]. In 2014, the average global atmospheric carbon dioxide level rose to 397.7 ppm, substantially higher than the 278-ppm floating in the atmosphere during the preindustrial time [6].

A sensors research that seeks to monitor indoor air quality (IAQ), VOCs and the lower explosive limit of combustible hydrocarbons (HCs) all become a target for developing new sensors to improve the quality of the air we breathe [7]. Sensors can be categorized as resistive sensors, surface acoustic

wave (SAW), quartz-crystal based sensors and also field effect transistor (FET) based sensors [8]. Resistive based sensors are most widely used due to the inherent advantage such as easy circuits and high sensitivity. Numerous researchers have shown one of the important parameters of gas sensors, many



**Fig. 1.** (a) Graphitic top-down approach and (b) molecular carbon precursor bottom-up approach for producing a wide variety of graphene based materials in large quantities [45].

papers about metal oxide gas sensors have focused and paid more and more attention to sensitivity and much effort has been made to enhance the sensitivity of gas sensors. It was observed that the film resistance increases or decreases in the presences of analyst gas depending on the type of semiconducting metal oxide used for preparing the sensors.

To the best of our knowledge, there were no special reviews about the factor influencing selectivity and sensitivity of the sensors parameter [9]. In the chemiresistive sensors, the selectivity is the most challenging issue in the diagnosis of diseases. Currently gas chromatography, mass spectroscopy and optoelectronic analysis have been adopted to detect the sub-ppm level of VOCs in exhaled breath. However, due to bulky devices size and complex measuring process these techniques are limited for use in real-time diagnosis. Metal oxide based chemiresistive gas sensors have been recognized as one of the most promising detecting tools for exhaled breath analysis in the diagnostic method. As the chemiresistive based breath analysis sensors offer greater usability for portable real-time diagnosis, low cost, easy fabrication and simplicity of operation [10].

Nanotechnology has been emerged to develop high sensitive biosensors and gas sensors in addition to inexpensive and low power devices proposing an alternative to silicon-based conventional technology that involves rigorous fabrication steps using a top-down approach [11-17]. The significance of CNTs and graphene materials arises due to a need for enhancing sensitivity and selectivity of chemicals and faster response time in very sensitive systems [18-23]. CNTs and graphene materials have become important due to their tunable characteristics to solve major issues related to low dimensional materials. Graphene has greatest possible surface area per unit volume while CNTs has high aspect ratios to adsorb chemical species. Due to unique one and two dimensional  $sp^2$ -bonded structure, both graphene and CNT have excellent electronic, mechanical, thermal and optical properties. [20-26].

A single layer graphene (SLG), few-layer graphene (FLG) and graphene oxide (GO) shows a drastic change in the electrical conductivity when exposed to the target chemical species to change the free electron concentration depending upon the donor or acceptor charge carrier on targeted species. Every atom of graphene is capable of interacting with even a single molecule of a target gas or vapors species as a surface atom which results in the better sensor response [27-31]. Thus, this review article aims to present an overview of chemical sensors based on next generation graphene and CNTs materials.

### Synthesis processes

One of the biggest challenges of science and technology today is the synthesis of nanoscale materials for large-scale production. The approach to

nanotechnology research and development are grouped into two categories, "TOP-DOWN" and "BOTTOM-UP". The "top-down" is an approach that downsizes materials from large-scale structures into nanometer-scale structures. There have been several synthesis methods for top-down approach such as thermal exfoliation [32], chemical exfoliation [33], sonication [34, 35], functionalization [36], while bottom-up approach consists of standard techniques such as CVD [37], epitaxial method [38], mechanical exfoliation [39] and Brodie's chemical oxidation method [40]. To tailor the atomic size, shape, stability, composition and edge structure in graphene and CNTs the most commonly chosen route for synthesis is bottom-up strategy [41]. Graphene is mostly obtained from graphite precursors on a relatively large scale through oxidation – exfoliation -reduction in the form of graphene oxide (GO) [42-45] as shown schematically in Fig. 1.

The GO structure contains abundant oxygen-rich functional groups such as hydroxide and epoxide groups on the basal plane and carbonyl and carboxyl groups on the edge of the graphene sheets. Generally, the oxidation and reduction create many defective sites on the graphene which offers an advantage in gas sensors application.

### Improved hummers method

The detailed synthesis procedure of GO powder from natural graphite powder using modified Hummer method has been reported in the past [46-48]. The synthesis of GO from natural graphite powder without using  $NaNO_3$  by modified oxidation reaction formula has been reported by Ji Chen *et al.* [49] The cost of GO synthesis was reduced by improved Hummers method as it eliminates the generation of toxic gasses and purifies the waste liquid by a simplified process. Several authors reported the synthesis of GO by using concentrated  $H_2SO_4$  and  $NaNO_3$  in the presence of  $KMnO_4$  which is capable of oxidizing natural graphite powder. However, there are still few drawbacks: 1) Releases of toxic gasses such as  $NO_2$  and  $N_2O_4$  during the oxidation procedures. 2) The process of filtrating GO from wastewater by removing the residual  $Na^+$  and  $NO_3^-$  ions creates difficulty during the synthesis process. With improved Hummer method, Ji Chen reported few advantages: 1) synthesis reaction of GO can be completed within few hours. 2) For improving the safety reaction and avoiding the evolution of explosive  $ClO_2$ ,  $KClO_3$  was replaced by  $KMnO_4$ . 3) The formation of acid fog was eliminated without the assistances of  $NaNO_3$ .

### Chemical vapour deposition (CVD)

Chemical Vapour Deposition (CVD) is the most promising technique for the synthesis of graphene films using transition metals as substrates with outstanding electrical conductivity and field effect

mobility properties [50]. This approach produces high quality and industrial scale graphene sheet by thermal decomposition of SiC [51], plasma enhanced [52], epitaxial growth of graphene on transition metals (Ni, Pd, Ru, Cu) Via CVD of hydrocarbons or alcohols [53, 54]. By decomposition of methane in the CVD reactors, single and few layer graphene (SLG and FLG, respectively) was successfully deposited on metal oxide surfaces. These metals act as a catalyst for decomposition of  $\text{CH}_4$  molecules but flow rate and temperature are extremely crucial for successful synthesis. There are several recent reports on the direct growth of graphene by decomposition of methane on noble metals like Rh, Ru, Pd, Ir, and Pt and also on some metal surface including Co, Ni, Cu [55]. However; there will not be any control over monitoring the number of layers or impurities arising during growth [37]. CVD is also the most promising method for industrial scale deposition of CNTs from microns to millimeters. Various techniques are employed for synthesis of CNTs such as laser ablation and ionic beam deposition [56, 57] and arc discharge [58]. However, laser ablation produces about 70 % by vaporizing a target graphite in a reactor at high temperature while using arc discharge, it yields only up to 30% by weight [59]. The higher aspect ratio between the tube length and diameter for CNT are grown at 700-800°C by chemical vapor deposition [18].

### Mechanical exfoliation

Mechanical exfoliation is an outstanding method to

focus on the problem such as uncontrollable defects, random size, and graphene produced with the random number of layer. The attempt for the synthesis of graphene by various mechanical exfoliations is reported by Min Yi and ZhigangShen [60]. Bottom-up techniques such as epitaxial growth and CVD can yield a high quality of graphene and CNTs with a small number of defects [61, 62].

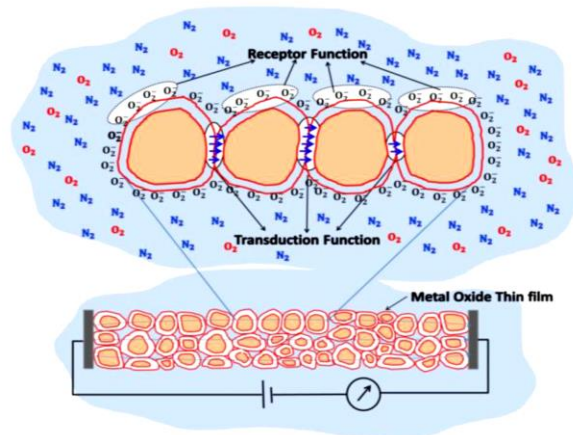


Fig. 2. Schematic representation of metal oxide thin film gas sensor [63].

### Gas sensors and sensing mechanism

The metal oxide gas sensor works on the principle of change in electrical conductivity or resistivity of the thin films on exposure to a target gas [63]. The resistivity or conductivity of the metal oxide films

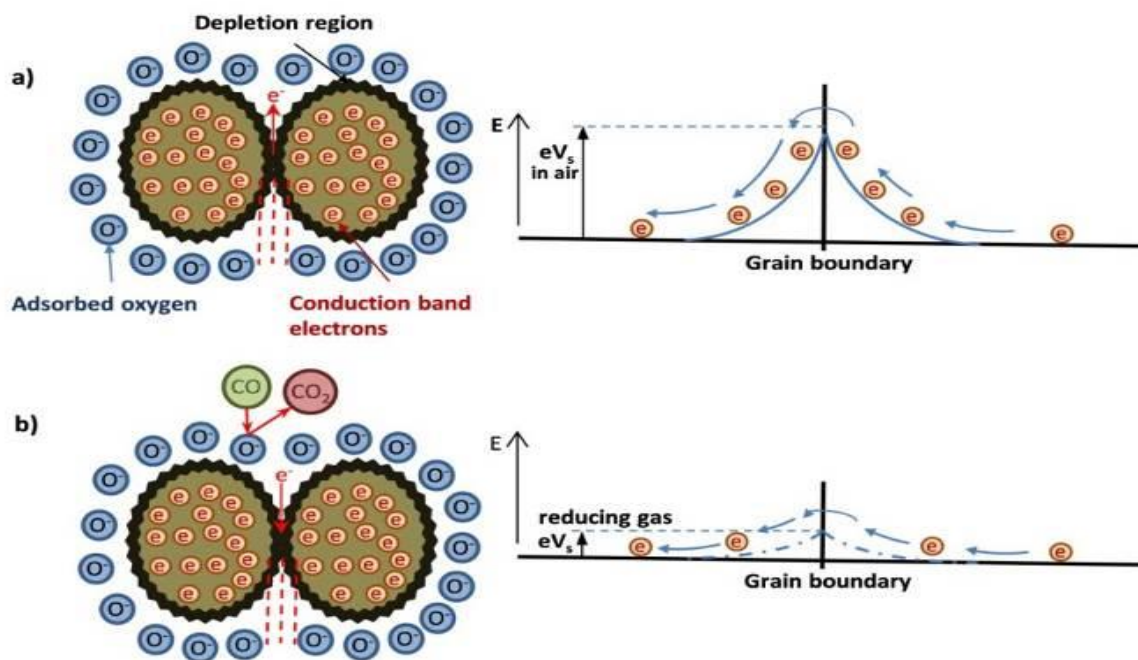


Fig. 3. Active sensing layer with numerous interconnected metal oxide grains [69].

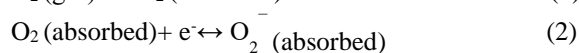
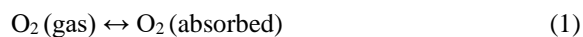
prepare high-quality, large-area graphene flakes but this method is extremely labour-intensive and time-consuming. However, it seems impossible to scale up for industrial production. In mechanical exfoliation, several issues still require a continuous

changes as the target gas molecules interacts with the metal oxide surface and act as either a donor or acceptor of charge carriers depending on target gas as shown in Fig. 2.



As a result, resistances of the metal oxide thin film increase or decrease depending upon the type of majority charge carriers in the semiconducting metal oxide films and the nature of gas molecules (i.e oxidizing or reducing gas) in an ambient atmosphere [64]. In n - type semiconductor, the majority charge carriers are electrons. When it interacts with a reducing gas an increase in conductivity occurs. On the other hand, an oxidizing gas depletes the charge carriers, leading to a decrease in conductivity. Similarly, in the case p - type semiconductor, where positive hole are the majority charge carriers, an increase in the conductivity is observed in the presence of an oxidizing gas.

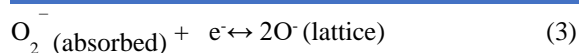
On the other hand, an increase in resistance is observed in the presence of reducing gas, where negative charge introduced into the material reduces the positive (hole) charge carrier concentration [65]. The variations in the depletion layer at the grain boundaries leads to the modulations in the height of energy barriers for the flow of free charge carriers in the presence of oxidizing/reducing target gas molecules resulting in a change in the conductivity of sensing materials of metal oxide semiconductor [66 - 68]. Thin film type gas sensors consist of an active sensing layer with numerous interconnected metal oxide grains as shown in (Fig. 3.). The absorption of O<sub>2</sub> forms oxygen ion species as O<sub>2</sub>, O<sup>-</sup>, O<sup>2-</sup> depending on the temperature by removing the charge carriers from the grains surface region and forms a depletion layer around the grain boundaries [70]. The surface characteristics of metal oxide materials and the oxygen partial pressure determine the depth of the depletion layer. The depletion layer on the grain boundaries becomes the bottlenecks results in a higher potential barrier for electric grain-grain transfer. This reaction lowers the oxygen species coverage and increases electrical conductivity by returns of free electron charge carriers to the bulk of the oxide material [71].



Several efforts have been made to improve the sensor performance for detecting various harmful chemicals such as NH<sub>3</sub>, NO<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S and SO<sub>2</sub>. [72]. Abha Misra *et al.* [18] demonstrated that gas sensitivity of NH<sub>3</sub> gas for CO nanoparticle coated on MWCNTs was enhanced twice compared to uncoated MWCNTs at room temperature and response time was 30 secs for detecting 7ppm of NH<sub>3</sub> gas. Yoon *et al.* [73] demonstrated that graphene devices sensors are more sensitive to CO<sub>2</sub> gas for detecting 10 to 100 ppm with the response time of 8-10 sec. Mitesh Parmar *et al.* [1] carried out a comparative study of toluene sensing behavior for graphene/Polyaniline (PANI) nanocomposite (G-PANI) and PANI. They found good sensor response for pure PANI (i.e. 12.6; 18.9; 38.4 % of sensitivity) while for G-PANI (i.e. 8.4; 11.6; 35.5 % of sensitivity) was decreased as the operating temperature increased from 30 to 100°C respectively. The response time for pure PANI was ~ 11 min and for G-PANI ~ 13 min at low operating temperature. The response time for G-PANI was reduced as compared to the pure PANI when the temperature was increased. Similarly, the recovery time was high for G-PANI (~ 27 min) compare to pure PANI (~24 min). With increasing operating temperature, the recovery time decrease than that of pure PANI. This high recovery time can be attributed to the inability for desorption of chemisorbed analyte. So far, various semiconductor-based gas sensors such as In<sub>2</sub>O<sub>3</sub> [74], SnO<sub>2</sub> [75], ZnO [76] and TiO<sub>2</sub> [77] have been proved as an efficient real-time method for formaldehyde (HCHO) and VOCs gas detection due to their inherent advantages such as low fabrication cost, high response, good thermal stability and easy construction of nanostructure based sensor. However, the high operating temperature resulting in high power consumption and difficulty in integration are major drawbacks that make metal oxide based gas sensors suffer for practical applications. Hence, the preparation of reliable, cost effective and the design of room temperature sensors are urgent in demand for commercial production [78].

**Table 1:** Comparison of various metal oxides hybrids with graphene, reduced graphene oxide, and CNTs based gas sensors.

Sr. No	Composite	Target Species	Operating Temp.	Range (ppm)	Sensor Response	Response Time	Recovery Time	Ref.
1	CO <sub>3</sub> O <sub>4</sub> -10wt% rGO	NO <sub>2</sub>	RT	60	Rs= 56%	1 min	2 min	[83]
2	ZnO- 10wt% rGO	NO <sub>2</sub>	RT	60	Rs= 36%	10 min	18 min	[86]
3	Graphene/SnO <sub>2</sub>	CO <sub>2</sub>	60°C	100	Rs=26%	8 sec	10 sec	[87]
4	Graphene/SnO <sub>2</sub>	NH <sub>3</sub>	200°C	75	Rs=38%	14 min	12 min	[88]
5	rGO/CNTs/SnO <sub>2</sub>	NO <sub>2</sub>	RT	5	S= 2.53	8 sec	10 sec	[89]
6	rGO/TiO	HCHO	RT	1ppm	Rs=0.64%	65 sec	112 sec	[78]
7	CeO <sub>2</sub>	HCHO	80°C	450	Rs=36.12	20 sec	12 sec	[90]
8	NiO	Ethanol	90°C	450	Rs=505	167 sec	130 sec	[91]
9	Graphene/SnO <sub>2</sub>	NH <sub>3</sub>	RT	50	S=15.9%	< 1 min	< 10 min	[92]
10	rGO/AgNWs	NH <sub>3</sub>	RT	100	S=15%	1 min	150 sec	[93]
11	GO	CH <sub>3</sub> OH	-	-	S=11.6%	10 min	-	[94]
12	ZnO/GO	CO	RT	22	ΔG=24.3%	5 Sec	5 Sec	[95]



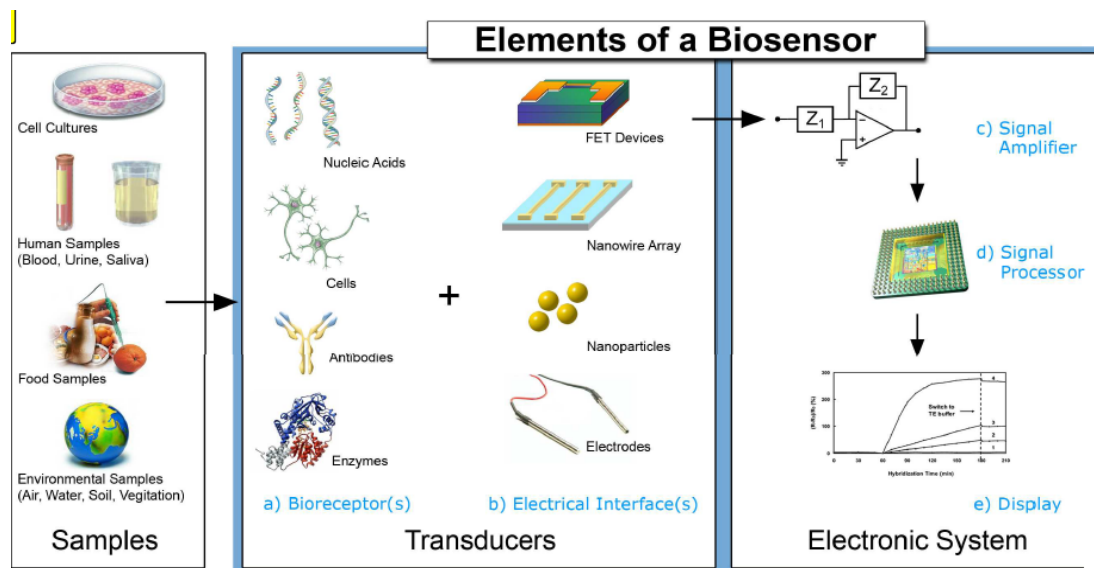
If VOCs detecting sensors can be operated at room temperature the cost and power consumption can be reduced [79, 80].

Hybrids rGO/TiO<sub>2</sub> based sensor exhibits 2 times higher magnitude of response to formaldehyde compared to the rGO [78]. Lu et. al. demonstrated that recovery response of the rGO based gas sensor could be significantly improved by thermal annealing of the rGO in argon at an optimum temperature (~200°C) [81, 82]. The spinal cobalt tetraoxide (CO<sub>3</sub>O<sub>4</sub>)–rGO composite based gas sensors investigated at room temperature showed a much higher response to NO<sub>2</sub> gas compared to rGO based sensors. Different rGO loading (0 to 30 wt %) was used onto CO<sub>3</sub>O<sub>4</sub> for fabrication of the sensor. However, the sensor using CO<sub>3</sub>O<sub>4</sub>–5 wt% rGO composite showed almost twenty times higher response than that of pure rGO based sensor whereas CO<sub>3</sub>O<sub>4</sub>–10 wt% rGO composite (Rs = 56%) showed higher sensor response (Rs) than that of ZnO – 10 wt% rGO composite (Rs = 36%) to 60 ppm NO<sub>2</sub> gas at room temperature [83]. SnO<sub>2</sub> is widely investigated to monitor hazardous NO<sub>2</sub> gas sensors but its operating temperature is above 100°C [84, 85]. Graphene /SnO<sub>2</sub> composite showed better response and recovery than MWCNTs/SnO<sub>2</sub> composites in lower concentration at room temperature for NO<sub>2</sub> gas. Fast and almost double response was observed at room temperature for graphene/SnO<sub>2</sub> composite (Rs = 9.6) compare to that of MWCNTs/SnO<sub>2</sub> composite (Rs = 4.5) and pure SnO<sub>2</sub> (Rs= 2.0) was detected for NO<sub>2</sub> gas for higher level of 20 ppm whose response time is less than 1 min and recovery time is less than 5 min. [86]. The comparative studies of graphene and CNTs as a composite with different metal oxides for room temperature detection of VOCs gas sensors are still in desired. Comparison of various metal oxides hybrids with graphene, reduced graphene oxide (rGO), and CNTs based sensors are given in Table 1.

## Electrochemical sensors

Aida Martin *et al.* [96] demonstrated improved electroanalytical performance using oxidized graphene nanoribbons (GNRox) and reduced graphene nanoribbons (GNRred) for the electrochemical sensors based on screen printed platforms not only compared to multiwall carbon nanotubes but also with carbon screen printed electrodes (CSPEs) shows an impressive chemical sensing of ascorbic acid (AA), Levodopa (LD) and Uric acid (UA). In author's opinion, overall selectivity of the analysis would be improved consequently by graphene materials due to induced electrocatalytic effect on the redox capacity of analytes. GNR- based electrochemical sensors opening novel avenues for fast and reliable UA assessment in the urine sample for POC testing application. Jianbo Li *et al.* successfully constructed the electrochemical sensors by a newly synthesized material based on  $\beta$ -cyclodextrin/ionic liquid/gold nanoparticles functionalized magnetic graphene oxide and applied on the glassy carbon electrode surface for determination of sunset yellow (SY) in spiked water sample, Mirinda drinks and minute maid [97]. In the field of electrochemistry [98, 99], molecular imprinting technology [100] has been introduced to improve the selectivity of electrochemical sensors. Molecularly imprinted polymer has recently become more research practicability in the chemical method because of low cost of preparation, high stability, high surface-to-volume ratio [101, 102]. However, in the field of sensors application, it has some drawbacks such as low density of imprinted sites, weak electrical conductivity and incomplete template removal, slow binding time [103, 104]. To overcome these disadvantages, new class of multifunctional nanomaterials molecularly imprinted electrochemical sensors were prepared which not only shown

Fig. 4. Elements and selected components of a typical biosensor [106].



enhancement in sensitivity but also great selectivity [105].

According to Shabi Abbas Zaidi *et al.* [107] from past few decades' electrochemical sensors categorized into enzymatic and non-enzymatic is the most common approach in nanotechnology for glucose sensors. However, many other enzymes have been utilized such as glucose dehydrogenase (GDH) [108, 109], and isoenzyme-2 of hexokinase [110]. Furthermore, few drawbacks are associated with these enzymes are low selectivity, poor thermal stability, high over potential which may be attributed to sluggish electron-transfer kinetics [111] and dehydrogenase enzyme has not proven feasible for electrochemical recycling [112]. Commercially available solid strip for test purpose most widely consists of GDH despite these disadvantages because GDH gets dissolves in oxygen independently. Gooding group has shown some detailed work on about GOx based glucose sensing articles [113, 114]. Recently, many researchers discuss the utilization of non-enzymatic base nanostructure for direct detection of glucose. Wu *et al.* demonstrated poly (sodium 4-styrene sulfonate) (PSS) non-covalently functionalized on MWCNTs or polyelectrolyte such as polyethyleneimine, (PEI) to template via in situ approach for facile and cost effective way to the synthesis of Cu NPs coated MWCNTs. The electrocatalytic sensitivity of modified MWCNTs/PSS/Cu exhibited better result compared to modified MWCNTs/PEI/Cu electrode owing to different loading content capacity of Cu NPs on MWCNTs [115]. By a simple electrochemical method without any substrate modification synthesized Ni(OH)<sub>2</sub> on carbon nanotube/polyimide (CNT/PI) was fabricated for non-enzymatic glucose sensors [116]. Enzymatic glucose sensors are most widely used as it owing high sensitivity, high selectivity, biocompatibility and cost effectiveness but challenge issue lying ahead is that it reduces the shelf-life and biofouling to some extent is a bigger problem [107]. Even though the non- enzymatic glucose sensors with nanostructures solved some of the problems but still sample dilution to accommodate sensors with operating conditions far from physiological PH or limited dynamic range

glucose sensors are most widely used as compared to non-enzymatic glucose sensors because of many limitations and hurdles. Thus, there is a need to get few very facile syntheses, selective, sensitive, stable and reproducible non-enzymatic approaches as recently under focus of vast scientific community and researchers [117]. Miniaturized devices capable of operating in complex systems are of great interest and graphene based materials are widely applied to fabricate such devices due to their super thin interfacial behavior and multi stimuli responses. Zipper like GO/poly (N-isopropyl acrylamide-co-diethyl amino ethyl methyl acrylate) composite interface was made to direct hierarchical self-assembly of GO and glucose oxidase and the interface showed on/off-switching when the pH was varied from 5-8. This was due to super hydrophilic to hydrophobic phase transition. Moreover, the interfacial bio-electrochemical properties were tunable during 20-40°C. Enzymes based programmable bio-electro catalysis is used to design switchable bioelectronics including biosensors and biofuel cells [118 - 120]. The switchable bio-electro catalysis are triggered by stimulus like temperature, pH, light, magnetic fields and potential [121] as well. In short, the stimuli-responsive polymer/graphene composite material enables the switching process and tunes the rate of zipper-like switchable catalytic reactions occurring on the electrode surface [107, 122]. Thus, these switchable zippers like graphene interfaces reveal new possibilities for bioelectronics, especially in the design and development of highly integrated super-thin, programmable bio-devices [123].

### Conclusion and future perspectives

This mini-review highlights merit and demerits of metal oxide composites used for the fabrication of sensors during the period spanning mid of 2010 to recent 2015. The problems overcome by the new generation of materials such as graphene and CNTs have been discussed. One of the key issues for commercialization of sensors is to fabricate disposable/reusable sensors with high sensitivity, selectivity, accuracy, fast response and recovery time

**Table 2.** Comparison of various metal oxides hybrids with graphene, and CNTs based biosensors.

S.No	Sample name	Sensor Analyte	Detection range	Reference
1	Graphene/PANI/AuNPs/GOx	Glucose	0.6 $\mu\text{M}$	[124]
2	Polydopamine/Graphene/GOx	Glucose	0.1 $\mu\text{M}$	[125]
3	Polymer/Graphene/PtNPs	Glucose	0.03 $\mu\text{M}$	[126]
4	Graphene/Pd/chitosan/GOx	Glucose	0.2 $\mu\text{M}$	[127]
5	Organic film/graphene	$\beta$ -lactoglobulin	0.001–100ng mL <sup>-1</sup>	[128]
6	MGF/GOx	E. coli O157:H7	7.8 $\times 10^3$ –7.8 $\times 10^6$ CFU mL <sup>-1</sup>	[129]
7	Au/Fe <sub>3</sub> O <sub>4</sub> /graphene	IgM	0.0375–18 AUmL <sup>-1</sup>	[130]
8	MWCNTs/GOx/NFE	Glucose	1.00 $\mu\text{M}$	[131]
9	CS/CNTs/ Au–PtNPs	Glucose	0.20 $\mu\text{M}$	[132]
10	MWCNTs	captopril	0.20 $\mu\text{M}$	[133]
11	PANI /MWNTs / $\beta$ -CD	dopamine	12.0 nM	[134]

does not seem practical. Commercially enzymatic

and high shelf-life which can possibly lead to the

limit of detection and real-time application onto small chips. The disposable electrochemical biosensors and gas sensors using the graphene and CNTs allows a fast response and recovery time, high sensitivity, selectivity, accurate and reproducible determination of sample. This work has been merely focused on the application of graphene and CNTs which opens the new possibility for easy biological screening as well as high sensitivity for the gas sensor at room temperature. This approach becomes highly promising from the point of view of care for fast and early diagnosis of the diseases and monitoring air pollution.

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