Nanomaterials as Toxic Gas Sensors and Biosensors

Jaison Jeevanandam, Abirami Kaliyaperumal, Mohanarangan Sundararam, and Michael K. Danquah

Contents

J. Jeevanandam
Faculty of Engineering and Science, Department of Chemical Engineering, Curtin University, Miri, Sarawak, Malaysia

A. Kaliyaperumal
Center for Environmental Studies, Anna University, Chennai, Tamil Nadu, India

M. Sundararam
Crystal Growth Centre, Anna University, Chennai, Tamil Nadu, India

M. K. Danquah (✉)
Chemical Engineering Department, University of Tennessee, Chattanooga, TN, USA
e-mail: michael-danquah@utc.edu

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Abbreviations

Al_2O_3	Aluminium oxide
AuNPs	Gold nanoparticles
BRET	Bioluminescence resonance energy transfer
CdSe	Cadmium selenide
CEA	Carcinoembryonic antigen
CeO_2	Cerium dioxide
CHS	Chondroitin sulfate
CNMs	Carbon nanomaterials
CNTs	Carbon nanotubes
CO	Carbon monoxide
CPE	Carbon paste electrode
CRET	Chemiluminescence resonance energy transfer
CTCs	Circulating tumor cells
CV	Cyclic voltammetry
DNA	Deoxyribonucleic acid
EIS	Electrochemical impedance spectroscopy
EMF	Electromotive force
FETs	Field effect transistors
Gly	Glyphosate
GO	Graphene oxide
GOx	Glucose oxidase enzyme
GR	Graphene
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulfide
Hb	Hemoglobin
hCG	Human chorionic gonadotropin
HOPG	Highly oriented pyrolytic graphite
IL-6	Interleukin-6
LbL	Layer-by-layer
MgO	Magnesium oxide
MnO_2 NPs	Manganese dioxide NPs
MNPs	Metal nanoparticles
MWNTs	Multi-walled carbon nanotubes
NADH	Nicotinamide–adenine dinucleotide
NH_3	Ammonia
NiOx	Nickel oxide
NIR	Near infrared
NO	Nitrogen oxide
NPs	Nanoparticles

PAH	Poly (allylamine hydrochloride)
PAni	Polyaniline
PEDOT	Poly (3,4-ethylenedioxythiophene)
PEG	Polyethylene glycol
PEI	Polyethyleneimine
PNA	Peptide nucleic acid
POC	Point-of-care
PPy	Polypyrrole
PSA	Prostate-specific antigen
PSS	Poly (styrene sulfonate)
PSS	Polystyrene sulfonate
Pt	Platinum
PTh	Polythiophene
PVP	Polyvinylpyrrolidone
QCM	Quartz crystal microbalance
QDs	Quantum dots
RNAs	Ribonucleic acid
SAW	Surface acoustic wave
SnO_2	Tin dioxide
SPANI	Poly (anilinesulfonic acid)
ssDNA	Single-stranded DNA
STW	Surface transverse wave
SWNTs	Single-walled carbon nanotubes
TiO_2	Titanium dioxide
TMF-α	Tumor necrosis factor-α
USD	United States Dollars
UV	Ultraviolet
VOCs	Volatile organic compounds
WO_3	Tungsten oxide
ZnO	Zinc oxide
ZnS	Zinc sulfide

1 Introduction

Sensors are the general term that is used for the materials that are used to detect and sense a physical parameter and converts them to electrical current (Pallas-Areny and Webster 2012). Sensors consist of four main parts, namely analyte or an element to be detected, receptor, transducer, and signal processing unit (Töppel et al. 2018). The analyte or the molecule to be sensed is the key for the fabrication of sensors, based on which the type of sensors to be used for detection will be decided (Ajay Piriay et al. 2017). The transducer is an essential component of a sensor, which converts the physical quantities into electrical signals (Kocakulak and Butun 2017). These converted electrical signals are amplified and converted into readable signals via signal processors, which can be displayed in a digital device (Erden et al. 2016). There are numerous types of sensors that are under extensive research and have been used in several applications (Khaydukova et al. 2017). Among these sensors, gas sensors are the widely utilized sensor type in several industries as well as in commercial markets (Dey 2018). In 2016, the overall market of gas sensors throughout the world is about USD 812.3 million, which is expected to be about USD 1297.6 million in 2023 (Bogue 2014). The expected growth in the gas sensor market between 2017 and 2023 is about 6.83%, which is based on the gas type, technology, geography, and end-use application (Markets 2017). Companies such as Amphenol Corporation (United States) and Figaro Engineering Inc. (Japan) are the significant producers of gas sensors for end-use applications including aerospace, medical, transportation, and residential safety (Kato et al. 2000; Shan et al. 2018).

Generally, micro-sized particles are utilized for gas sensor fabrication to monitor distinct gas molecules that are toxic to humans above its threshold limit value (Lupan et al. 2016). These micro-sized particles exhibited enhanced potential in sensing various toxic gases and help to avoid their exposure toward humans (Acosta et al. 2009). However, the lack of precision in the detection, disability in detecting multiple gases, and formation of impurities during the detection of gases are the limitations of using micro-sized particles for detection of gases (Carregal-Romero et al. 2013; Kim and Kim 2014). Thus, nano-sized particles and materials are introduced as novel materials to fabricate gas sensors (Llobet 2013). These nanomaterials possess exclusive size-dependent entities with an elevated ratio of surface and volume as well as effects due to confinement in the quantum regime (Eranna 2016). Additionally, the size, morphology, and surface charge of the nanosized materials can be manipulated based on the desired sensor applications (Lyson-Sypien et al. 2015). These advantages of nanomaterials pave the way for a separate market for nanomaterial-based toxic gas sensors which are now gaining attention among industries and researchers (Šutka and Gross 2016).

The emergence of nanotechnology has led to the fabrication of biosensors, similar to toxic gas sensors (Pandey et al. 2008). These biosensors are the latest trend in biomedical sciences which is beneficial in detecting any form of biological analytes (Rai et al. 2012). The advantages of nanomaterials in toxic gas sensors have made the biomedical scientists to try out nano-sized particles for the fabrication of biosensors (Mishra and Rajakumari 2019). The incorporation of nanomaterials in biosensors has led to various wearable and in-situ biochip advancement that can help in the detection of biological analytes and in the diagnosis of diseases (Chandra and Segal 2016). Currently, the global market of biosensors is about 21.2 billion USD, which is expected to reach about 31.5 billion USD in 2024 (Markets 2019). Due to the high demand for novel toxic gas and biosensors, numerous nanomaterials are introduced to fabricate sensors with high detection efficiency (Mehrotra 2016).

Metal, metal oxide, carbon and polymer nanoparticles, either in nanoformulated or nanocomposite forms are the nanomaterials, that are usually utilized for sensor fabrication in recent times. The diverse variety of nanomaterials used in the sensor fabrication has led to the development of semiconductor (Dey 2018), sensitive (Wang et al. 2016a), hybrid (Chatterjee et al. 2015), fluorescent (Zhou et al. 2016), room temperature (Shafiei et al. 2015), and impedimetric (Vignesh et al. 2015) sensors to detect toxic gases. Likewise, microbial (Ponamoreva et al. 2019), electrochemical (Rotariu et al. 2016), surface plasmon resonance (Olaru et al. 2015), whole-cell based (Saini et al. 2019), and lab-on-a-chip (Jamshaid et al. 2016) are the distinct biosensors that are fabricated using nanomaterials. Thus, the aim of the present chapter is to discuss about nanomaterials that are used to fabricate sensors with the ability to detect toxic gases and biological molecules. In addition, the drawbacks of nanomaterials as sensors, and the efficiency and limitations of green synthesized nanomaterials for sustainable, toxic gas detection, and biosensing applications are also discussed.

2 Nanomaterials as Toxic Gas Sensors

Nanomaterials are widely utilized to fabricate swift-responding nanosensors with electrochemical, optical, thermal, piezoelectric, and other properties for low concentration chemical compound detection (Tallury et al. 2010). Recently, nanomaterial-enhanced sensors such as carbon nanotubes, nanosized metal particles (particularly gold and silver), graphene, semiconductors, quantum dots, and silicon-based nanomaterials were tailored for detecting and measuring contaminants such as ions of heavy metals, hydrogen peroxide (H_2O_2), organophosphate pesticides, toxic gases, and industrial wastewaters (Su et al. 2012). Metals, oxides of metals, metal complexes, polymers, and carbon-based nanomaterials are extensively under research for the fabrication of toxic gas sensors.

2.1 Metal and Metal Oxide Nanomaterials

2.1.1 Metal Oxide Nanomaterials

Numerous metal oxide nanomaterials are reported to be appropriate for reducing, combustible, or oxidizing gas detection via measurements of modifications in conductivity. It has been proven that the oxide nanomaterials show a sensitive conductivity response upon detecting a gas molecule (Kanazawa et al. 2001). It is noteworthy that the choice of metal oxides for fabricating a gas sensor is based on their electronic structure. The oxides of metals possess an inclusive electronic structure range that is classified into oxides of transition metals and non-transition metals, which are further subclassified into oxides of pre-transition metals and post-transition metals. Oxides of pre-transition metals, such as MgO, are naturally inert, due to their hefty gaps in their electronic bands, which makes it tedious to form electrons or holes. These materials are infrequently designated to fabricate gas sensors as it is hard to measure their electrical conductivity (Kanazawa et al. 2001). The oxide materials of post-transition metals can alter their properties to perform as a better toxic gas sensors. Thus, these materials are reported to be highly sensitive than oxides of pre-transition metals toward the environment. Nevertheless, instability in structures and difficulties in optimizing parameters of these nanomaterials limits their usage in conductometric gas sensor applications. Only oxides of transition metals with electronic configurations of d0 and d10 are employed in real gas sensor application. The configuration of d0 is present in binary oxides of transition metals, whereas the configuration of d10 exists in the oxides of post-transition metals. Even though, several semiconductor oxides of metals that are delicate to noxious gas molecules are reported to be n-type semiconductors. Also, it was demonstrated that certain p-type semiconductors are also utilized as materials to fabricate gas sensors. It is reported that about 10% content of NiOx is required to alter n-type into p-type conductivity. When temperature elevates, an increase in the sensitivity of n-type film toward reducing gases can be noted, which is vice versa in p-type NiOx film (Wisitsoraat et al. 2009). Thus, semiconductors of p-type nature can operate in a comparatively lesser temperature than n-type, for toxic gas sensor applications.

Sensors that are fabricated with semiconductors of metal oxides are primarily applied to sense-gas molecules via target gas and surface oxygen mediated redox reactions (Yamazoe and Shimanoe 2008). This process requires two initial steps, namely (1) redox reactions, where scattered oxygen ions over material surface will react with target gas molecules to create electronic variations in the surface of oxides; and later (2) the disparity is transferred via transduction into a noticeable change in the electrical resistance of sensors. The variations in resistance can be noticed by determining the capacitance alterations, function of work function, optical characteristics, mass, or reaction energy (Kanan et al. 2009).

Tin dioxide is a noteworthy metal oxide nanoparticles that are used for toxic gas detection. It is a granular n-type material with density-dependent electrical conductivity of surface pre-adsorbed oxygen ions. It is reported that the tin dioxide resistance alters, depending on the variations in the gas concentration (Batzill and Diebold 2005; Wang et al. 2010), with nonlinear association between concentration and resistance of target gas. Also, other semiconducting oxides of metals such as tungsten trioxide are generally utilized for noxious gas detecting applications. Oxides of tungsten nanomaterials as anode that are fabricated via electrochemical tungsten etching illustrate outstanding hydrogen and nitrogen oxide detection responses (Endres et al. 1996). However, the pure WO_3 respond poorly toward NH_3 with declined selectivity, due to the interference of NOx. Thus, vanadium and copper decorated WO_3 are utilized as additives of catalysts to recover their response, eliminate anomalous sensor performance and to utilize WO_3 in gas sensors (Hoefer et al. 1997). Other nanosized metal oxides (TiO_2) are highly beneficial as layers of sensitivity to elevate dielectric permittivity of sensors to adsorb gas molecules

(Fraiwan et al. 2011). Likewise, distinct ZnO nanostructures including nanowires, nanobelts, and tetrapods are fabricated as monitoring devices for ultrasensitive H_2S and NO gas detection (Gupta et al. 2010).

Moreover, semiconducting sensors of metallic oxides that are fabricated using nanomaterials are gaining importance in large-scale applications. However, elevated operational temperature demand in certain sensor involves high budget and intricate arrangements than other room temperature sensors, which limits their large-scale application. Researchers have developed a unique method to overcome these limitations, which includes silicon-based integrated circuit fabricated microsensor mediated micro-heater technology (Lee et al. 1996). Additionally, pulsating operating temperature mode to heat at short intervals (Jaegle et al. 1999) was also introduced, which simplifies the sensor operation and reduces the consumption of power. Further, studies about nanosized oxides of metal structures have revealed that semiconductor nanowires can recover the response time and sensitivity of gas sensors (Comini 2006). Another challenge is the requirement of extended recovery period after exposure of each gas, which restricts their employment in certain e-nose like sensor devices, as the concentration of gas is rapidly and regularly under modifications. Moreover, the defects and instability in the structure of indicators also reduce the applications in the field of sensors. In recent times, there are numerous reports to prove the efficiency of metal oxide nanomaterials in detecting toxic gas molecules with high sensitivity (Dey 2018). However, novel solutions are required to overcome the limitations and defects of semiconducting oxides of metals, which is achievable via extensive sensor research in the future.

2.1.2 Metal Nanoparticles

Nanosized metal particles are deposited over substrate surface for elevating the ratio between area and volume and also to favor the adsorption of gas molecules. When these nanomaterials are bound with analyte, the molecules of analytes alter their substrate entities as gas molecules are adsorbed to the metal (Jimenez-Cadena et al. 2007). Mostly, the preparation for deposition is performed via metal precursor vaporization, to afford consequent annealing of the nanofilms or particles. For instance, an electromotive force (emf) measuring electrode in a cell with high concentration of oxygen was fabricated using a zirconium and yttrium metal component along with 5–10 nm-sized iridium nanoparticles. In the existence of oxygen at 650 °C, the sensor conductivity was altered within 10–20 s of response time. The sensor response was explained via oxidization reaction, where the nanosized iridium particles permit a better interface between the substrate and the molecules to provide an enhanced contact area for the analyte (Kimura and Goto 2005). Li et al. (2002) fabricated an electrode of platinum with surface embedded nanosized gold particles along with a silver–silver chloride composite as a reference electrode. The nanosized metal particles are reported to be beneficial as a layer of sensors to permit the detection of hydrogen and sulfate analytes with ultrahigh sensitivity and selectivity at low temperature (Li et al. 2002). Moreover, gold and platinum nanoclusters are widely accepted as a catalyst to upsurge sensor sensitivity. Generally, nanoclusters are integrated or fabricated into alloys with distinct nanomaterials to enhance their sensitivity, selectivity, and to increase their kinetic oxygen reduction limitation (Hallil et al. 2010). Further, Wang et al. (2010) prepared an extremely sensitive hydrogen gas nanosensor using platinum nanocluster-decorated graphene oxide (GO) between a prepatterned pair of titanium–gold electrodes with microgap (Xiang et al. 2010). Currently, there are several nanomaterials, especially biosynthesized nanoparticles, are employed in the fabrication of toxic gas nanosensors (Xu et al. 2018b). It is noteworthy that most of the studies reported the utilization of metal oxide nanomaterials, rather than a nano-metals, to fabricate substrates of nanosensor to detect toxic sensors. However, the utilization of nanosized metal particles on the substrate with inert molecules to fabricate noxious gas nanosensors should be studied extensively in the future.

2.1.3 Nanosensors with Metal Complexes

Transition metal nanomaterials are proficient in modifying interactions of atoms which makes them to be extensively beneficial as receptors to detect and analyze various gases. This behavior is subjugated to prepare an analyte with complex supra-molecules for selectivity enhancement of numerous toxic gas sensors. Elosua et al. (2006) stated that optical fiber sensor fabricated by coating gold and silver complex was used to detect volatile alcoholic compounds. Nanoscale Fizeau interferometer with complex alcoholic vapor dopants is proved to possess vapochromic property to act as recognition layer of the nanosensor. The solvents coordinate with centers of silver metal and break the silver and gold–silver bonds to provide initial orange to red color to the complex. The results revealed claim the nanosensor with metal nanoparticles can be used for at least 3 months without degradation for the effective detection of toxic gases (Elosúa et al. 2006).

Brousseau et al. (1997) revealed carbon dioxide detection using reactions of carbon dioxide with hydroxysilanes, alcohols, and amines under optimum pressure and temperature. The study utilized three bifunctional nano-receptors along with a group of amines that coordinates with ions of metal in the copper octane di-yl bis (phosphonate) thin film and are coated over a microbalance made up of quartz crystal. The sensor and the analyte reaction at optimum temperature were reversible which is highly dependent on the receptor and the concentration of carbon dioxide (Brousseau et al. 1997). The primary benefit of metallic sensing layer complexes as sensing layer is the interactions that are reversible between the devices and the analytes. The formation of coordination bonds in gas detection are fragmented by temperature increment or chemical alterations in the sensor. Besides, specific receptors are intended to cooperate with precise analytes to increase their selectivity. Thus, fabrication of sensors with these complexes is expensive and is used only to functionalize specific receptors that can be beneficial as nanostructured transducer materials (Jimenez-Cadena et al. 2007).

2.2 Polymer Nanomaterials

Polymers are used in gas sensor fabrication as they possess exceptional physicochemical properties and are classified into polymers with conducting and nonconducting properties.

2.2.1 Conducting Polymers

Polymers with electric conductive property are broadly considered as toxic gas sensors due to their sensitive electrical conductivity alterations via assorted inorganic and organic gas exposure. This property has led to critical material examination for fabricating layers that can detect gas molecules in sensors (McNaghten et al. 2009; Shrivas et al. 2007). Polymers with conducting property such as polyaniline (PAni), polypyrrole (PPy), polythiophene (PTh), and their byproducts are widely employed as noxious gas determining nanosized materials. It can be noted that pure polymers with low conductivity to perform as an individual gas determining material. Hence, extended research to select specific polymers for nanocomposite fabrication with metallic nanoparticles is highly recommended in the future. Earlier reports demonstrated that polymer conductivity is upgraded via exclusive doping approach by reactions of protonation or redox. Later, polymers are converted into conductors or semiconductors after the reversible doping process. It is significant to note that the level of doping can be altered via chemical-based target gas and polymer reactions, making the analyte detection to be a more practical with conducting polymers. Several polymers are doped through redox reactions and specific polymers are utilized for gases, which are inactive at room temperature to redox reactions. For instance, redox reactions will not happen in CO at room temperature, however, PAni can lead to a change in their redox potential (Hatfield et al. 1994). Thus, conducting polymer-based nanomaterials are directly used as transducers in toxic gas detecting nanosensors to reflect electrical property modifications.

2.2.2 Nonconducting Polymers

Polymers without conducting property are broadly employed as absorptive coatings on diverse sensor devices, where general polymeric transducers with distinct physisorption are used as sensor fabricating material. For example, layers of polymer that lead to resonance frequency modifications, enthalpy, and dielectric constant upon analyte desorption or absorption are coated on the surface of surface transverse wave (STW), quartz crystal microbalance (QCM), calorimetric sensor devices, capacitive and surface acoustic wave (SAW) for sensitive toxic gas detection. Later, these sensor devices are transformed into an output electrical signal via monitored polymer properties (Bai and Shi 2007). Even though the basic polymer with nonconducting principles are logical in gas sensors, their recital is highly intricate, even after coating them on the sensor devices. For example, STW devices with resonance property are coated with sensitive thin nanosized layers of polymer to feature extensive rewards of relative sensitive gas probing, inclusive electrical property, and low sensor oscillator noise than bulk counterparts of SAW (Hagleitner et al. 2002). Furthermore, membrane of polymer with nonconducting properties was also proved to be utilized in semiconducting oxides of metal-based gas sensors as sieves of molecules, to augment their inclusive selectivity for sensitive layers of polymer introduction (Avramov et al. 2000).

Numerous approaches have been reviewed for polymer nanocomposite fabrication with exclusive properties for sensor applications (Kaushik et al. 2015). Among several approaches based on emulsion polymerization such as conventional emulsion, soapless emulsion, microemulsion, suspension, dispersion, and precipitation polymerization approaches (Wong et al. 1995), mini-emulsion polymerization is considered as a potential approach to fabricate functional and flexible nanomaterials (Anderson and Daniels 2003). Nohria et al. (2006) utilized a thin film of poly (anilinesulfonic acid) (SPANI) to construct a sensor to evaluate humidity. The 90 nm sized thin films were deposited via the spin coating method or by the layer-by-layer (LbL) nanoparticle assembly approach, which added negative charges on the coupled layer polycation substrate and a polyanion named poly (allylamine hydrochloride) (PAH), and poly (styrene sulfonate) (PSS), respectively. After the deposition of layers, the PSS is substituted by SPANI to yield a film with 26 nm of thickness. When these nanofilm sensors are under atmospheric exposure, its resistance declines with an increase in relative humidity along with 15–30 s of response time (Nohria et al. 2006).

Nanosized gas sensors with polymers have merits such as enhanced sensitivities at reduced response times, compared to bulk polymers. Furthermore, sensors with polymers function at room temperature, which make them superior than metal oxide nanoparticles as they detect toxic gases at elevated temperatures. Therefore, the lower consumption of energy by nano polymers permits their utilization in toxic gas detection units that are operated by batteries. Additionally, advantages including the low fabrication cost, simple structures, and portability, as well as reproducibility (Landfester 2006) make these nanostructures to gain focus of researchers to use them in nanosensor fabrication. Gas sensors with polymers also possess hindrances such as instability, poor selectivity, and irreversibility. Further, the performance can be altered due to the working environment. Besides, there are only few evidences to explain the actual working principle of toxic gas-sensing polymers. Despite these demerits, polymer-based nanosensors can be used as a lower power-consuming toxic gas sensors in the future.

2.3 Carbon-Based Nanomaterials

Carbon nanotubes (CNTs) and graphene show a high potential for miniaturized chemical sensor development, due to their excellent large surface-mediated adsorptive capacity, better electrical property modulation upon exposure to analytes via greater cross-sectional interaction zone, capability to fine-tune electrical nanostructure entities by tailoring their composition or size and the configuration ease into distinct geometries (Goustouridis et al. 2005; Munoz and Steinthal 1999). SWNTs are cylinders with individual diametric layers of 1–3 nm and micron length of rolled graphite. Similarly, multi-walled carbon nanotubes (MWNTs) are fabricated via concentric SWNTs with various nanosized diameters. Both SWNTs and MWNTs are employed to fabricate various sensors, due to their exclusive physico-electronic properties (Ellis and Star 2016). The adsorption processes are highly favored due to their unique atomic arrangement on SWNTs surface and their enhanced ratio between area and volume, which increases their sensitivity to various gas molecules in the atmosphere (Zaporotskova et al. 2016). Nanotubes can exhibit both metallic and semiconductor properties with their extraordinary electrical conductivity which depends on their structural chirality (Kavitha and Kalpana 2017). Semiconducting nanotubes are highly beneficial in device construction including field-effect transistors (FETs). These nanotube devices are utilized for analyte determination via electrical surface conductivity modifications of CNTs (Tran and Mulchandani 2016). This can lead to consequences such as, transfer of charge from analyte to the nanotube, or may elevate the scattering potential of analyte (Park et al. 2017a). These exclusive effects of CNTs are utilized for electrode of third gate-mediated FET device modulation (Jang et al. 2016). Alternatively, the current will decline without altering the CNTs characteristics, if the center of scattering is an analyte. Even though CNTs possess sensitivity toward the surrounding chemical environment, they lack selectivity which is a major limitation to use them in large-scale sensor application. Thus, several functionalization processes have been implemented for sensitivity and selectivity enhancement of CNTs as gas sensors. Among functionalization processes, distinct polymeric material coating and doping or oxides and metal particle deposition are proven to be significant in improving the gas detection properties of CNTs at room temperature (Lee et al. 2018).

Gas sensors with graphene and pristine CNTs have firm restrictions, such as low analyte sensitivity, declined selectivity, irreversibility, and long recovery time (Bekyarova et al. 2004). Graphene and CNTs functionalized with diverse materials are essential to overcome the limitations of free CNTs via chemical property modifications and sensing performance enhancements. Functionalization is significant in altering the chemistry of carbon nanotubes and graphene and manipulating their chemical properties is highly essential for utilizing them in potential applications including sensor fabrication (Dong et al. 2004). There are numerous CNTs and graphene functionalization approaches that are reported in literatures (Wright 2017) such as defect method, covalent sidewall functionalization approach, noncovalent exohedral, and endohedral functionalization. CNTs functionalized with metal, metal oxides, and polymer nanoparticles can result in improved electronic properties, selectivity, and response to specific gases through target molecule interface with functional additives is distinct, compared to free and bulk carbon materials (Li et al. 2011).

2.3.1 Carbon Nanotubes Functionalized with Metal, Metal Oxide, and Polymer Nanomaterials

The conductivity of nanotubes can be altered significantly with sidewall functionalization of chemical reactants, which is essential to specific gas sensor application. Various approaches have been reported for covalent carbon nanotube functionalization such as creation of defect site and functionalization via defects, embedding acids of carboxyl group on caps of carbon nanotube end and following acid derivatization. Polymer surfactant nanotube wrapping for noncovalent functionalization is proven to reserve the physical entity and solubilization of nanotubes. Pure carbon nanotubes do not possess appreciable sensitivity toward certain gases, whereas CNTs decorated with nanoparticles comparatively improves gas-sensing performance. Nanosized metal particles including platinum, lead, aluminium, and tin are widely utilized to decorate CNTs, allowing determination of selective gases, such as H_2, NH_3, NO_2, and CO (Fowler et al. 2009; Li et al. 2010; Stankovich et al. 2006; Yan et al. 2010). The oxide of metal NPs modified with CNT as hybrid was developed as sensing films that displayed advantages such as high catalytic activity, efficient charge transfer, and capacity to adsorb. Numerous studies have demonstrated the brilliant sensing ability of CNTs/SnO_2 and CNTs/ZnO hybrid sensors for carbon monoxide, nitrogen dioxide, and ammonia gas detected at low temperatures (Ma et al. 2012). Polymer-functionalized CNTs also considered as an essential nanomaterial to recover the CNTs and polymers of organic nature's compatibility in sensor fabrication and provide ultrahigh sensitivity and selectivity for the determination of gases. The unique characteristics of CNTs combined with polymer properties such as delocalized bonds, high permeability, and low density have established the possibility of detecting diverse gas molecules with swift response, excellent sensitivity, and great reproducibility (Alshammari et al. 2017). In addition, various other CNT modifications via doping or coating are recommended to further augment the CNT's gas-detecting properties (Gardner and Bartlett 1993; Penza et al. 2008).

2.3.2 Graphene Functionalized with Metal, Metal Oxide, and Polymer Nanomaterials

In several gas-sensing applications, metal nanoparticles are embedded with graphene to upsurge the sensitivity, detection limit, selectivity, or a mixture of all these properties (Kim 2009). In several cases, graphene nanomaterials are modified via electrochemical metal salt reduction by using graphene flakes that are attained from oxide of graphene. In specific scenarios, the deposition of nanosized particles over graphene can be achieved via chemical metal salt reduction by adding reducing agent, followed by that are yielded after adsorption of nanosized particles in solution (Liu et al. 2011). Noble metals that are active as catalysts are extensively utilized to elevate graphene-based chemical sensor sensitivity toward a wide range of gases. Lately, the advancement of room temperature-operating sensors with oxides of metal along with enhanced sensitivity and truncated fabrication cost has fascinated much consideration. When molecules of gases are adsorbed on the surface of functionalized oxides of metal with graphene sensor film, nanosized oxide of metal particles act as sensing and element of transduction ability, whereas oxide of graphene act as a mesh with high conductivity. These nanomaterial-based sensor intensifies their transducing property resulting in larger alterations in conductance, compared to previous results demonstrated for chemical synthesized graphene-based sensors (Bekyarova et al. 2004). Numerous literatures also reported that the graphene is incorporated into matrices of polymer to yield novel nanosized composites. It was recommended that graphene nanosheets can provide highly active polyaniline nucleation sites and exclusive electron transfer pathways (Yuan and Shi 2013).

2.4 Nanocomposites

Generally, gas sensors are fabricated by two types of materials such as organic polymers with conductivity and inorganic oxides of metals. Gas sensors using coveted functional and conductive organic conducting polymers are proven to improve gas-detecting performance (Castro et al. 2011). Although these nanocomposites are unstable and exhibit comparatively meager sensitivity (Janata and Josowicz 2003) due to excellent polymers with conducting and affinity property toward environmental moisture and volatile organic compounds (VOCs). Gas detectors fabricated via oxides of inorganic metals exhibited upsurge detecting qualities due to oxygen-mediated stoichiometric alterations and surface-active electrical charges (Capone et al. 2000). The function of these devices at higher temperatures led to gradual modifications in metal oxide nanostructure properties. The high-temperature function can lead to grain boundary fusion, which can alter nanostructure stability and shorten the sensor lifetime. In addition, high-temperature operating nanocomposite sensor needs a discrete assembly of temperature-controlled heating complex and consumes extra heating power. The shortcomings of organic materials such as low stability and conductivity, and inorganic materials such as functioning at high temperatures and sophisticated processability act as a hurdle to be employed in large-scale gas sensor fabrication. Thus, the nanocomposites are utilized to promote effective and peculiar gas-sensing ability and allow them to operate at low temperature. A promising approach for conductometric gas sensor improvement is to utilize composite nanomaterials that are fabricated via semiconducting metal oxide or metal or carbon nanoparticles along with organic polymer or inorganic matrix (Barsan et al. 2007).

Suri et al. (2002) described that nanosized magnetic composites possess a significant part in noxious gas sensor applications. Nanosized composites of iron oxide and poly pyrrole that are prepared via instantaneous polymerization and gelation process were utilized for the fabrication of sensors to determine humidity. The results revealed that these sensors are highly beneficial in toxic gas determination such as carbon dioxide, nitrogen, and methane. Further, the study also stated that the sensitivity of nanosensor was in the order of carbon dioxide > nitrogen > methane, due to their kinetic diameter variation of gas molecules (Suri et al. 2002). Moreover, various methods are utilized to combine CNMs with polymers to yield functional nanocomposites with specific extraordinary properties for technological purposes (Yu et al. 2017). Polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymers are exploited as matrices to integrate various CNMs (Xue et al. 2017). The polymer matrices embedded with carbon nanomaterials are an attractive approach for combining their electrical and mechanical entities (Liu and Kumar 2014). These novel nanosized composites created novel chances, not only in sensor applications, but also in electrochemical capacitor, solar cells, transistors, and molecular electronic devices (Christ et al. 2017). In recent times, nanosized composite with carbon polymers, and nanosized metal particles (MNPs) with unique alignments and proportions are broadly examined (Kondratiev et al. 2016; Monerris et al. 2016). Further, Trakhtenberg et al. (2012) reported numerous metal oxide nanocomposites that are utilized to fabricate efficient nanocomposites for the sensitive and selective determination of noxious gases in the environment at room temperature (Trakhtenberg et al. 2012). All these studies revealed that nanocomposites can be an excellent nanosensor fabrication material for gas sensor applications, compared to free nanoparticles.

3 Nanomaterials as Biosensors

Similar to toxic gas sensors, biosensors are also fabricated using metal, metal oxide, carbon, polymer, and composite nanomaterials.

3.1 Metal and Metal Oxide Nanomaterials

The noble metals including gold, silver, and platinum (Pt) are commonly utilized in the field of biosensor application. These metal nanoparticles (MNP) are significant in detecting microorganisms such as viruses, bacteria, and pathogens with enhanced sensitivity and specificity. These MNPs incorporated biosensors with biological recognition receptors namely antibody, enzyme, nucleic acid, and cells are also utilized for formidable disease monitoring applications such as cardiovascular and cancer diseases. The MNPs act as mediators to transfer the signals that are obtained via modification on their surface to transducers in the form of electrochemical, piezoelectric, and optical signals. The gold NPs are in conjugation with primary or secondary antibodies through gold–antibody ionic interaction, hydrophobic interaction, and dative binding phenomena. Conjugation of nanoparticles with antibodies is achieved via other chemical interactions such as thiol derivative chemisorption, bifunctional linkers, and via adapter molecules namely Streptavidin and biotin (Ijeh 2011; Ljungblad 2009).

3.1.1 Glucose Biosensors

The MNPs are conjugated with a glucose oxidase enzyme (GOx) and ferrocyanide for the glucose sensor signal enhancement. The most popular techniques for conjugation are amperometry, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). The nanosized gold particles are attached covalently to GOx and CV measurement is used to obtain the quantitative biological glucose level in complex samples. Similarly, the ferrocyanide acts as a mediator for transferring electrons during GOx reaction for glucose detecting nanosensors. A typical example of the fabrication of the glucose sensor with nanosized gold electrode particles was demonstrated by Zhang et al. (2005) to detect highly concentrated with enhanced sensitivity and 8.2 μM limit of detection (Zhang et al. 2005). Likewise, nanosized platinum particles are incorporated with GOx and Nafion on the highly oriented pyrolytic graphite (HOPG) surface to fabricate sensors with stability, controllability, and reproducibility. The results showed that these nanosensors exhibited a linear response (25 μM) with 15 mM limit for determining glucose (Liu and Huang 2012). Similarly, manganese dioxide NPs (MnO_2 NPs) were also conjugated with Nafion and GOx on the graphene nanoribbon surface under the influence of 0.1 M phosphate buffer at pH 7.4. The amperometric glucose measurement for the nanosensor prepared with MnO_2 NPs at an operating potential of +0.50 was reported to be as high as 56.32 μA/mmol cm^2 (Vukojević et al. 2018). However, the detachment of GOx from the Nafion is common in the preparation, which is the major limitation for glucose biosensor fabrication. Thus, these challenges can be avoided by treating the initial electrode with positively charged polyethyleneimine (PEI) polymer, which was followed by adding 5% (w/v) of negatively charged Nafion on the PEI surface. Later, GOx has to be attached to the PEI/Nafion layer to initiate strong bond formation between them (Tsiafoulis et al. 2005). Furthermore, selenium nanoparticles are conjugated with mesoporous silica composite (MCM-41) matrix. In this study, the carbon paste electrode (CPE) was bound together with mesoporous silica composite material which was later attached to selenium nanoparticles to embed on the MCM-41 surface. Since GOx reaction liberates the electron, the amperometric measurement will yield the quantity of glucose present in the sample by slight modifications in the surface of MCM-41 that are initiated by selenium metal (Yusan et al. 2018).

3.1.2 DNA Biosensors

Nanosized gold and silver particles are widely utilized in DNA biosensor fabrication to detect the target DNA molecules. Metallic nanoparticles possess the ability to bind with target DNA molecule at 0.1 M of sodium chloride concentration, due to the salt aggregation effect. Further, an increment in the salt concentration to the 2 M of sodium chloride concentration will lead to aggregation of ssDNA molecules with NPs (Jamdagni et al. 2016). On the other hand, the peptide nucleic acid (PNA) and PNA–DNA bound with NPs are measured at 600 nm and 520 nm, respectively, in a UV–visible spectroscopy, which indicates the colorimetric DNA sensing ability of gold–silver nanoparticles (Kanjanawarut and Su 2009). The alterations in the DNA motif via gold NP are based on the pH variation in fluorescent quenching method (Liu et al. 2006). In this scenario, the DNA hybridization determination is possible via gold nanoparticles encapsulated by streptavidin and biotinylated oligomer target by stripping potentiometric method (Madhurantakam et al. 2018). Additionally, gold NPs linked with cysteamine-modified electrode that are encapsulated with oligonucleotide and a group of mercaptohexyl at the 5′-phosphate of DNA end and chitosan layer onto SAM-modified gold NPs are highly significant in electrochemical biosensor fabrication to detect target DNA (Mazloum-Ardakani et al. 2015).

3.1.3 Blood Pressure Sensors

A simple and common method for monitoring blood pressure is to use piezoelectric sensors that detect the pressure of blood flow in vessels, based on piezo resistivity, capacitance, and piezo electricity mechanism. Nanosized metal particles including gold, aluminium, silver, and copper are considered as the best materials for the fabrication of integrated circuits to be included in piezoelectric sensors (Xu et al. 2018a). Conversely, nanosized gold–copper alloy particles are used for uric acid determination, depending on an enzymatic reaction through electrochemical measurement (Wang et al. 2001). Moreover, the electro-catalytic effect of silver with platinum nanoparticles on reduced oxide of graphene is utilized for tumor necrosis factor-α (TNF-α) detection through electrochemical measurements (Pingarrón et al. 2008). It is noteworthy that TNF-α is an essential part of proinflammatory cytokines which is associated with salt-sensitive hypertension and is related to renal injury (Mehaffey and Majid 2017).

3.2 Carbon-Based Nanomaterials

The hollow cavity in carbon nanotubes (CNTs) attracts several researchers to use them in the fabrication of nanosized biosensors (Adhikari and Chowdhury 2010), as hollow cavities provide a chemically inert environment (Khlobystov et al. 2005; Manzetti 2013). Further, these hollow cavities also provide a potential electromagnetic or a magnetic response site for biosensor and nanoreactor development via electric or electromagnetic impulses (Khlobystov 2011). The CNT structures are classified according to the molecule of interest such as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) via binding to their biosensor surfaces. However, SWCNTs with one carbon layer can easily transfer an electric signal after an analyte or mediator molecule attachment to their modified surfaces (Hirata et al. 2008).

CNTs are accepted as a potential material for electrochemical biosensor fabrication, owing to their enhanced electron transferability to the electrodes. Thus, CNTs are reported to be working on both second and third electrode systems using the electrochemical cell, which converts or transfers a biological element detection into electrochemical signal. However, the hydrophobic nature of CNTs and strong intermolecular p–p interactions are the major limitations, while developing CNT-based biosensors (Thirumalraj et al. 2017; Wang and Dai 2015). For instance, cationic surfactants effectively bind with negatively charged DNA for designing functionalized CNTs. In addition, cationic functionalities are introduced with amine groups to allow further attachment of other targeting molecules and fluorophore markers to track cells. Several studies demonstrated that RNAs, short double-stranded and single-stranded DNAs, possess the ability to dissolve into SWCNTs, whereas the macromolecules are attached to the open MWCNTs cavity in a nonspecific fashion (Sanz et al. 2011). Furthermore, water-soluble, PEGylated phospholipid functionalized SWCNTs were developed for cancer drug delivery and as a noninvasive diagnostic tool (Liu et al. 2008). In addition, MWCNTs conjugated with poly ethylenimine to enhance binding properties of DNA and these conjugated nanoparticles are proved to be highly sensitive and low toxicity for efficient detection and targeted delivery of genes (Liu et al. 2005).

Graphene sheets with high surface area are fabricated into semi-conductive films and conductive interfaces to be useful in biosensor development. Graphene-dependent biological sensors are broadly utilized in medical diagnostic applications. These biological sensors are utilized in the determination of significant biomolecules including cytochromes, reduced nicotinamide–adenine dinucleotide (NADH) form, hemoglobin (Hb), and individual amino acids (Kuila et al. 2011; Song et al. 2012). Further, these biosensors are involved in trace element detection that are present in urine samples (Tahernejad-Javazmi et al. 2018). Graphene-based biosensors also possess ability to detect heavy metals and larger biomolecules including DNA (Huang et al. 2015a; Mishra et al. 2017).

3.3 Polymer Nanomaterials

The polymeric nanoparticle-based biosensors are highly beneficial compared to metal and ceramic materials due to their mild synthetic conditions, scalable downstream processing, flexibility, low operating temperature, nontoxic, and biocompatibility. It can be noted that the conducting polymers are proven to possess high sensitivity, precise reproducibility, and eliminates nonspecific binding with the analytes in biosensors (Park et al. 2014). The macroscale hydrogel-based materials are durable, elastic, transparent, and biocompatible for the prosthetic device fabrication such as wearable or even implantable biosensor devices. Poly (3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), polypyrrole (PPy), and poly indole are the general conducting polymers that are employed in biosensor fabrication. These nanosized polymers are conjugated with CNTs, MNPs, metal oxides, and other nanomaterials to enhance their sensitivity and selectivity while detection biomolecules (Annabi et al. 2014; Oliva et al. 2017). The polylactic acid (PLA) and PLA–alginate nanoparticles are efficiently encapsulated platinum–porphyrin complex for oxygen detection based on fluorescent measurement. A linear fluorescence response of oxygen concentrations (0–6 mM) was recorded with sensitivity toward oxygen indirectly measures and represents the presence of 0–10 mM of glucose within 4 seconds via catalytic reaction. These biocompatible and implantable glucose biosensors are proposed to be highly beneficial as in-situ glucose sensors for diabetic patients (Pandey et al. 2019). Moreover, the glyphosate (Gly) herbicide was detected via p-aminothiophenol-functionalized AuNPs with Gly as a template molecule that is fabricated using the electro-polymerization technique. The study emphasized that a linear sweep voltammetry with $[Fe (CN)^6]^{4-}$and $[Fe (CN)^6]^{3-}$ solution can be utilized for the quantitative detection of 1 pM and 1 μM concentration of Gly, respectively (Do et al. 2015).

The template-oriented nanosized polymer particles are utilized in innumerable forms including porous membranes, vesicles, micelles, and macromolecules for biosensor applications. The mesoporous conducting nanocomposite polymer of micro-sized flowers of graphene-nanosized polyaniline fibers (PANInf-GMF) was reported to be beneficial in cholesterol biosensor fabrication. This polymer material was placed over the glass substrate that is coated with Indium–tin oxide via drop-casting approach and this novel biosensor electrochemically sensed cholesterol with a 1.93 mg/dL as limit of detection (Lakshmi et al. 2016). Similarly, PPy was used for the electrochemical enhancement of skeletal muscle cell proliferation, whereas PEDOT and polystyrene sulfonate (PSS) were utilized for the detection of dextran sulfate. The conjugation of PPy, PEDOT and PSS as a nanomaterial was used in the fabrication of biosensors with enhanced conductivity that can increase skeletal cell differentiation and helps in monitoring in vitro dextran sulfate (Harman et al. 2015). Likewise, PANIs are formed via polymerization with a chiral monomer chondroitin sulfate (CHS) for chondroitin sulfate detection (Yuan and Kuramoto 2004). The incorporation of bio-dopants namely chondroitin sulfate, dextran sulfate, and alginate, into polymers of PEDOT are further used to detect biomolecules such as proteins, fibronectin, and collagen (Molino et al. 2014). Other studies with PPy and PANI showcased that the polymeric nanoparticles can be utilized to detect cell proliferation and dextran sulfate, respectively (Gilmore et al. 2009; Yuan and Kuramoto 2003). In addition, most biosensors fabricated via polymer are utilized for peptide and protein determination. For instance, a potentiometric biosensor for urea determination was developed via a copolymer conductive thiophene, and poly (3-hexylthiophene-co-3-thiopheneacetic acid). The urease-immobilized polymer film electrode was covalently surface linked with carboxyl group of polymer film to detect urea with a detection range of about 1–5 mM (Lai et al. 2017).

3.4 Nanocomposites

The construction of biosensors with nanocomposites provides additional reinforcement for the signal transaction and to use them in diverse applications. The nanocomposites are broadly classified into four types such as metal, ceramic, polymer, and magnetic composites. The metallic composites of rare earth elements are further divided into bimetallic colloids. Metallic oxides, including Al_2O_3 and MgO in combination with other metal oxides, CNT and platinum, iron, magnesium, and nickel bimetallic colloids in combination with other metals including ruthenium, copper, palladium, and silver (Janas and Liszka 2018; Khalil et al. 2018). The bimetallic nanocomposites are exclusively used in implantable biosensor preparation as they possess specific biological entities such as diffusion coefficient, biocompatibility, and biodegradation rate. It also helps in eliminating infected cells with the influence of external magnetic field (Pankhurst et al. 2016).

The graphene (GR)- and graphene oxide (GO)-based nanocomposites show high conductivity of electricity, enhanced area in the surface, defective site access, and better activity as electrocatalysts. These properties of GR and GO make them as a highly efficient material to fabricate nanocomposite-based biosensors. The functional groups of oxygen present in the GO are hydrophilic and hence, have high binding efficiency with MNPs, oxides of metals, nanosized semiconducting particles, polymers, and quantum-sized dots to recover their biosensing electrochemical ability. The nanocomposite-based biosensors are broadly classified into three types are enzymatic, nonenzymatic, and immunosensors, which is based on the type of biomarkers to be detected and the desired applications. The biomarkers such as hydrogen peroxides (H_2O_2) and DNA are detected using GO-based nanocomposite biosensors. The P-L-His–reduced GO and CeO_2–reduced GO is used for H_2O_2 detection, whereas, chitosan–GO, GR–reduced GO and gold NPs–reduced GO are beneficial for DNA detection. It can be noted that GR and reduced GO-based nanocomposites are extensively utilized for glucose biosensor fabrication. Most of the enzymatic reactions in humans are demonstrated to be based on NADH-dependent reactions. These NADH molecules are detected through nanocomposites that contain gold and silver NPs with reduced GO such as gold NPs–reduce GO–PAH (poly (allylamine hydrochloride)), and gold–silver NPs–P(L-Cys)–ErGO. Further, the cholesterol molecules are detected with nanocomposites of GR and reduced GO, apart from gold, palladium, and platinum, the additional molecules in blood serum are detected by other nanocomposites that consist of chitosan, TiO_2 nanowires, PPy (polypyrrole), and PVP (polyvinylpyrrolidone) (Istrate et al. 2016; Komathi et al. 2016; Pakapongpan and Poo-Arporn 2017; Pramanik et al. 2018; Radhakrishnan and Kim 2015; Tığ 2017; Vilian and Chen 2014; Wu et al. 2017; Zou et al. 2019).

Besides, graphene-based nanocomposite biosensors are employed for dopamine, bilirubin, ascorbic acid (AA), and uric acid (UA) determination via nonenzyme electrodes that are fabricated using multilayer graphene nanoflake films (MGNFs) (Shang et al. 2008; Thangamuthu et al. 2018). It is reported in various literatures that nanocomposites of GR and reduced GO with metal or metal oxides are highly beneficial in glucose, H_2O_2, and cholesterol sensors (Dhara et al. 2015; Gao et al. 2014; Lakshmi et al. 2016; Zor et al. 2014). Further, the graphene-based nanocomposites are used to develop immunosensors for biomarker determination such as human chorionic gonadotropin (hCG), carcinoembryonic antigen (CEA), interleukin-6 (IL-6), and prostate-specific antigen (PSA). The early detection of breast cancer markers such as ERBB2c and CD24c is quantified through gold–graphene oxide nanocomposites. Moreover, the tumor cells were identified by bio-probe that is fabricated via GO–polyaniline (PANI) nanocomposites along with CdSe quantum dot-functionalized polystyrene microspheres (Saeed et al. 2017; Wang et al. 2018). Similarly, graphene-coated gold and silver NPs as nanocomposites are used to determine CEA antigen (Huang et al. 2015b). Likewise, electrochemical label-free immunosensor was fabricated to sense PSA via nanosized chitosan–graphene–methylene blue composite (Yáñez-Sedeño et al. 2017). Also, circulating tumor cells (CTCs) were captured from the blood via graphene oxide conjugated with Neutravidin to restrain and detect the biotinylated epithelial cell that is adhesive to antibody (Yoon et al. 2013). Recently, Saeed et al. (2017) produced nanosized graphene oxide–gold composites modified with DNA aptamer (ERBB2c and CD24c) for early breast cancer detection. A sandwich-type strategy to build sensor was utilized for fabrication which has led to sensitive detection of ERBB2 and CD24 (Saeed et al. 2017). In addition, Wang et al. (2018) demonstrated that CdSe quantum dot-functionalized polystyrene microspheres can be used as a bio-probe along with GO–polyaniline (PANI) nanocomposites for ultrasensitive tumor cell detection. The results revealed that the detection limit was about 3 cells/mL, which was attributed to the high rate of electron transfer and enhanced loading of tumor cell on the surface of nanosized composites (Wang et al. 2018).

3.5 Other Novel Nanomaterials

The nanomaterial-based biosensors are showing promises to determine molecules and are in high demand in the current pharmaceutical market. The current scenario seems to be challenging to enhance the electrochemical sensors for real-time measurement, point-of-care (POC) analysis, portability, and direct analysis of multiple target analytes. Nanomaterials have been employed as immobilized bioreceptor, electrode modifiers, and electroactive labels, to increase the direct or indirect signals for the detection and quantify biomolecules (García-Mendiola et al. 2018). Since nanomaterials possess an enhanced surface area, the biomolecules are attached to the electrodes via physical adsorption through van der Waals forces (Yáñez-Sedeño et al. 2017). Thus, the biomolecules are immobilized to either supramolecular or coordinative binding biological species surfaces. For instance, SWCNT are coated with poly (adamantane–pyrrole), which is anchored to glucose oxidase (GOX) and gold nanoparticles are bound to β-cyclodextrin. The adamantane-tagged GOX was immobilized over the novel nanomaterials for the glucose biosensor fabrication and the glucose was measured by the potentiostatic method at 0.7 V (Holzinger et al. 2009).

The luminescent semiconducting nanocrystals are called as quantum dots (QDs), which are predominant nanomaterial that are used for the biosensor fabrication. The in vitro immunoassays-based biosensors are fabricated via quantum dots for nucleic acid determination via fluorescence resonance energy transfer (FRET) method. The core-shell CdSe–ZnS QDs with size-tunable fluorescence entities are used for live tracking of cell, in vivo imaging, drug discovery, and other biological diagnostic purposes (Michalet et al. 2005). The bioluminescence resonance energy transfer (BRET) principle for QD655-Luc8 determination is reported to be useful for in vivo imaging of endogenous chromophores (So et al. 2006). The effective sensing of biomolecules using FRET and BRET is based on graphene oxide (GO) with quantum dots (QDs) quenching approach (Dong et al. 2010). The DNA and oligonucleotide are detected through FRET quenching, which reveals the optical transduction of QD (Freeman et al. 2013). The principles of FRET and BRET are used along with quenching approach to transfer charges and chemiluminescence resonance energy transfer (CRET) as light-mediated transducers for certain biosensing purposes with QDs (Algar et al. 2010). Further, streptavidin-conjugated QDs are utilized in the imaging of prostate-specific antigen (PSA) and ssDNA via near-infrared (NIR) light using surface plasmon resonance phenomena (Malic et al. 2011). Moreover, the ferromagnetic iron oxide nanomaterial is mostly used in the determination of numerous bio-analytes such as DNA, mRNA, proteins, enzymes, drugs, pathogens, and tumor cells (Haun et al. 2010).

4 Nanomaterials as Sustainable Gas and Biosensors

It is noteworthy from the previous sections that the nanomaterials are extensively utilized in the fabrication of enhanced toxic gas and biosensors. However, the toxicity and stability of nanomaterials toward humans and the environment are a major concern, while utilizing them in sensors (Jeevanandam et al. 2018). Several literatures reported that chemically synthesized nanomaterials are toxic to human cells and organs, irrespective of the type, concentration, or dose (Khan et al. 2017). Chemical-based nanomaterial synthesis approaches utilized toxic precursors, stabilizing and reducing agents, which encapsulate over nanomaterials to exhibit toxicity toward human cells (Andra et al. 2019). These toxic nanomaterials are impossible to be used as implantable biochips and other biomedical applications (Darwish et al. 2019). Even in toxic gas sensors, it is better to avoid toxic nanomaterials as they may lead to hazard effects toward the environment after its lifetime (Valsami-Jones and Lynch 2015). Thus, green or biosynthesis approaches are introduced for the fabrication of nanomaterials to be used as sensors (Mandal et al. 2018). These biosynthesized nanomaterials are formed by using biomolecules and hence they are less or nontoxic to human cells, compared to chemically synthesized nanomaterials (Yola et al. 2014). The recent trends in sensor applications are to utilize biosynthesized nontoxic nanomaterials for the fabrication of sustainable sensors that are not harmful to both humans and the environment (Omobayo Adio et al. 2016).

Additionally, the energy used to fabricate sensors with green synthesized nanomaterial is much lesser compared to sensors derived from a chemical synthesis approach, which makes them as a significant method to develop sustainable sensors (Sharma et al. 2017).

4.1 Metal-Based Nanomaterials

Numerous metal, metal oxide nanoparticles, and nanocomposites were synthesized via green synthesis approach for the fabrication of efficient and sustainable toxic gas sensors. Pandey et al. (2013) fabricated an eco-friendly nanosized gold particle via reducing agent from the extracts of guar gum. These green-synthesized nanosized particles were employed as an optical sensor to detect aqueous ammonia via surface plasmon resonance. The obtained results emphasized that the green-synthesized gold nanoparticles possess properties of good reproducibility, excellent sensitivity with less than 10 s response time, and detection limit of 1 parts-per-billion (Pandey et al. 2013). Likewise, Zhao et al. (2015) synthesized spherical shaped, 6–10 nm-sized zinc oxide nanoparticles coated with silver using leaf extract from *Tribulus terrestris* to be used as a nontoxic and economic gas sensor at room temperature. The study revealed that the silver-coated zinc oxide nanoparticles possess enhanced and sustainable ethanol gas-sensing properties than pure zinc oxide nanoparticles (Zhao et al. 2015). Moreover, Li et al. (2008) fabricated porous tin dioxide nanoparticles by using an innovative ionic liquid template at room temperature named 1-hexadecyl-3-methylimidazolium bromide using a biogenic sol–gel approach. The obtained micro and mesopore nanoparticles were employed to detect gases such as carbon monoxide and hydrogen. The result revealed that the tin dioxide nanoparticles have the potential to be a sensitive and swift responding sustainable gas sensor (Li et al. 2008). Silver nanoparticles synthesized using ultraviolet radiation (Dubas and Pimpan 2008), *Cyamopsis tetragonaloba* (Pandey et al. 2012) and gold nanoparticles via locus bean gum (Tagad et al. 2014) are the other green synthesized nanomaterials that possess the ability to be fabricated as sustainable gas sensors.

Recently, Kalanur et al. (2015) fabricated palladium–tungsten oxide nanocomposites via polyvinyl pyrrolidone as a template using ultraviolet radiation-assisted photochemical method, without using any toxic chemicals. These green-synthesized metal nanocomposites exhibited excellent gas-sensing ability against hydrogen with excellent sensitivity (Kalanur et al. 2015). Likewise, Manoj et al. (2018) introduced novel green method to synthesized monodispersed copper nanoparticles using carboxymethyl cellulose. These green synthesized copper nanoparticles were combined with multi-walled carbon nanotubes and glassy carbon to detect nitrite oxidation. The result revealed that the novel nanocomposite possesses excellent nitrite oxidation detection property with great sensitivity (Manoj et al. 2018). Moreover, Tomer et al. (2019) reported that the silver nanoparticles fabricated via cyanobacterial extracts possess enhanced ammonia sensing ability (Tomer et al. 2019). Similarly, silver nanoparticles synthesized via *Duranta erecta* extract (Ismail et al. 2018), silver nanoparticle decorated carbon nanotube (Banihashemian et al. 2019), and palladium-deposited multi-walled nanotubes (Yoo et al. 2019) are the other significant green synthesized nanomaterials that are employed for sustainable toxic gas sensor fabrication.

Apart from toxic gas sensors, green-synthesized metal nanoparticles are also used to fabricate biosensors. Zhang et al. (2013) synthesized hybrid membrane structures of nanosized gold-reduced graphene oxide particles using uric acid, glucose, ascorbic acid, and dopamine as reducing agent to be beneficial as a hydrogen peroxide sensor. The result emphasized that the self-assembled hybrid membranes possess enhanced hydrogen peroxide detection potential with high selectivity, stability, and low detection limit (Zhang et al. 2013). Likewise, Liu et al. (2012a, b) reported a novel biogenic nanosized gold particles–graphene sheet nanohybrids using polyoxometalate as a reducing and encapsulating agent. The result demonstrated that the nanohybrids possess elevated catalytic activity with better sensitivity, stability, swift response, varied range of linearity, and low limit of detection (Liu et al. 2012a). Meanwhile, silver–graphene nanocomposites were synthesized via reducing tannic acid. The electrochemical and the Raman scattering results emphasized that the nanocomposites possess surface-enhanced Raman-scattering properties with enhanced hydrogen peroxide detection ability. The study confirmed that the nanocomposites can be used as an enzyme-less, amperometric hydrogen peroxide and glucose sensor with rapid response time of less than 2 s (Zhang et al. 2012b). Moreover, silver nanoparticles as optical fiber-based hydrogen peroxide sensors (Tagad et al. 2013), palladium-decorated poly(3,4-ethylenedioxythiophene) as a nonenzymatic biosensor to detect hydrogen peroxide (Jiang et al. 2013), biotemplated synthesized gold nanoparticles—bacteria cellulose nanofiber nanocomposites (Zhang et al. 2010), starch-stabilized silver nanoparticles (Vasileva et al. 2011), *Sargassum alga* synthesized palladium nanoparticles (Momeni and Nabipour 2015) are greener nanomaterials that are used in sustainable biosensor fabrication.

In recent times, Gayda et al. (2019) listed the metallic nanoparticles that are attained via biogenic method and used as a biosensor construction platform (Gayda et al. 2019). Bollella et al. (2017) fabricated nanosized gold and silver particles via reducing quercetin for biosensor applications. These spherical shaped, 5–8 nm sized, green-synthesized nanoparticles showed enhanced efficiencies as third-generation lactose biosensors (Bollella et al. 2017). Meanwhile, Su et al. (2016) fabricated nanostructure of cobalt oxide hydroxide using a photochemical approach without template, surfactant, or toxic solvents of organic nature at optimum temperature. The result showed that these nanostructures are highly beneficial in the sunlight mediated bifunctional detection of hydrogen peroxide and can be used to fabricate novel biosensors (Su et al. 2016). Silver-reduced graphene oxide–carbon nanotube nanocomposites were fabricated recently via a novel green synthesis approach for the biosensor applications. The result demonstrated that the nanocomposite with unique sensing properties exhibited excellent ability to detect dopamine with a response time of 12 s and 0.033 μM of detection limit (Khan et al. 2016). Similarly, green synthesized zinc oxide nanoparticles (Muthuchamy et al. 2018), graphene nanoribbon–silver nanoparticle–polyphenol oxidase composite

(Sandeep et al. 2018), gold nanoparticles (Raj and Sudarsanakumar 2018), cyclodextrin-capped gold nanoparticles (Zhang et al. 2019), and molybdenum disulfide–gold nanoparticles (Wu et al. 2018) are the other recent nanomaterials that are used to develop sustainable biosensors.

4.2 Carbon-Based Nanomaterials

Similar to metals, carbon-based nanomaterials were also used to fabricate toxic gas and biosensors. It is noteworthy that most of the carbon-based nanomaterials are nanocomposites as carbon materials are highly reactive and cause toxic reactions toward humans and microbes. Nanosized composites of tin dioxide with reduced graphene oxide to detect nitrogen dioxide at low temperatures (Zhang et al. 2014), graphene–zinc oxide nanoparticle hybrid (Kavitha et al. 2012) and conjugated polymer–carbon nanotube (Dai et al. 2002) are widely used in the gas sensor applications. However, they are synthesized via chemical approaches that use toxic chemicals and are not suitable for biosensor applications. Nanosized sheets of graphene decorated with nanosized zirconia particle hybrid for the enzyme-less detection of methyl parathion (Gong et al. 2012), indium-doped tin dioxide nanoparticle-graphene nanohybrids as nitrogen dioxide sensors (Cui et al. 2013), tin dioxide nanoparticle-decorated graphene sheets as cataluminescence gas sensors (Song et al. 2011), and mesoporous spherical tin dioxide–graphene nanocomposites as highly sensitive formaldehyde sensor (Chen et al. 2016) are the carbon-based nanomaterials that are used as sustainable gas sensors. In recent times, zinc oxide loaded with nanosized silver particles along with reduced graphene oxide are designed as hybrid for low-temperature detection of acetylene gas (Iftekhar Uddin et al. 2015), *Justicia glauca* leaf extract synthesized graphene oxide reduced with nanosized silver particle decoration as nitrobenzene sensor (Karuppiah et al. 2015), graphene-based sensors (Wang et al. 2016c), and nanosized hybrid composite of iron oxide-reduced graphene oxide to detect nitrogen dioxide at room temperature (Zhang et al. 2017) are the latest graphene-based nanomaterials that are used in sustainable toxic gas sensor fabrication. Likewise, carbon nanotubes (Davis et al. 2003; Wanna et al. 2006) and nanodots (Sun and Lei 2017; Wang et al. 2016b) were also synthesized via green approaches and are used to fabricate sustainable gas sensors.

Several green synthesized carbon-based nanomaterials were also employed for biosensor fabrication. Nayak et al. (2013) demonstrated a novel green synthesis method for the fabrication of nanosized hybrid of graphene-carbon nanotube decorated with zinc oxide particles as composites using solar energy. These novel nanohybrids were subjected to perform as a transducer in an organophosphorus biosensor and the result revealed that the nanohybrids exhibited a linear Paraoxon detection response of 1–26 nM with a detection limit of 1 pM (Nayak et al. 2013). Likewise, a biogenic nanosized composite film that is fabricated with glucose oxidase, gold particles, polyvinyl alcohol, and carbon nanotubes by Zhang et al. (2011). The result from the study reported that the nanocomposite exhibited a linear amperometric response toward concentration of glucose (0.5–8 mM) with a sensitivity of 16.6 μA mM^{-1} cm^{-2} (Zhang et al. 2011). Similarly, nanosized composites of gold reduced graphene oxide were synthesized via aqueous extract of rose flower as reducing agent. These novel green synthesized nanocomposites exhibited enhanced efficiency to be an effective glucose sensor with a low (10 μM) limit of detection (Amouzadeh Tabrizi and Varkani 2014). Recently, carbon dots (Liu et al. 2015), nickel–cobalt oxide–graphene nanohybrids (Ko et al. 2017), photoluminescent self-doped carbon dots (Wang et al. 2017), carbon dots-manganese dioxide nanosheets (Qu et al. 2017), and composites made up of nanosized silver particle, reduced oxide of graphene and carbon nanotube (Lorestani et al. 2015) are synthesized using green methods and are used to fabricate sustainable biosensors.

4.3 Polymer-Based Nanomaterials

Polymer nanomaterials and individual nanomaterials functionalized with polymers were widely used to fabricate toxic gas and biosensors. Venditti et al. (2013) introduced an innovative osmosis-based method for polyaniline–gold nanoparticle fabrication. Further, these nanocomposites are doped with hydrogen sulfide to detect ammonia gas and the result demonstrated that these nanomaterials possess enhanced sensitivity against ammonia up to 10 parts-per-million, compared to other vapor organic compounds (Venditti et al. 2013). Moreover, Nia et al. (2015) reported that assembly of silver nanoparticle decorated graphene oxide over glassy carbon electrode via an amperometry method. Polypyrrole nanofibers were attached to the electrodes and are employed as nonenzymatic hydrogen peroxide sensor. The result showed that these nanocomposites possess enhanced ability to detect gases with a detection limit of 1.099 (Moozarm Nia et al. 2015). Likewise, Wang et al. (2008) produced antimony-doped tin dioxide nanoparticles via a new block copolymer with amphiphilic property named poly(ethylene-*co*-butylene)-*block*-poly (ethylene oxide). These doped nanoparticles were employed to detect formaldehyde gas in the atmosphere and the nanoparticles exhibited good and swift responses in detecting the gas with good recovery (Wang et al. 2008). In recent times, conducting polymer–nanoparticle composite based chemo-electrical gas sensors (Park et al. 2017b), zinc oxide thin film prepared with inorganic green sodium–carboxymethyl cellulose polymer as acetone sensors (Muthukrishnan et al. 2016), uniformly decorated silver nanoparticles on polypyrrole as hydrogen peroxide sensor (Nia et al. 2015) and polyaniline–samarium-doped titanium dioxide nanocomposites (Ramesan and Sampreeth 2018) are the green synthesized polymer nanomaterials that are used to fabricate sustainable toxic gas sensors.

Huang et al. (2011) fabricated a bio-electro-chemically active infinite coordination polymer nanoparticles and reported that they possess enhanced glucose detection property (Huang et al. 2011). Likewise, Zhang et al. (2010) synthesized nanocomposites via nanosized gold particles and bacterial cellulose nanofiber for hydrogen peroxide detection with 1 μM of detection limit (Zhang et al. 2010).

Similarly, Asati et al. (2009) fabricated a polymer-coated nanosized cerium oxide particles for oxidation monitoring in cells and antioxidants (Asati et al. 2009). Moreover, Liu et al. (2012a, b) synthesized a nanodot polymer with doped nitrogen that is rich in carbon and with photoluminescent property for biosensor applications, especially for the label-free copper ion detection in body fluids (Liu et al. 2012b). Furthermore, Ruan et al. (2013) described a green synthesis approach for polydopamine–graphene composite film fabrication that is modified with enzyme electrode to be useful as a glucose sensor (Ruan et al. 2013). In recent times, novel carbon nanotube–poly (brilliant green), carbon nanotube–poly (3,4-ethylenedioxythiophene) as enzyme-based biosensors with electrochemical property (Barsan et al. 2016), gold nanoparticles stabilized by alcohol oxidase protein that is encapsulated with polyaniline as amperometric alcohol biosensor (Chinnadayyala et al. 2015) and silver nanoparticle embedded in bacterial cellulose nano-paper as plasmonic sensors (Pourreza et al. 2015) are the novel green synthesized polymeric nanomaterials that help in sustainable biosensor fabrication.

4.4 Novel Nanocomposites

Nanocomposites are the latest addition to the broad set of nanomaterials that are effective for sensor applications. Punicalagin green functionalized copper–copper oxide–zinc oxide nanocomposite as potential electrochemical transducer (Fuku et al. 2016), nanosized composites of graphene oxide reduced by zinc oxide for nitrogen dioxide gas-sensing application (Kumar et al. 2015a) and tin dioxide-based hierarchical nano-microstructures (Jiang et al. 2009) are the novel nanocomposites that are extensively under research as sustainable toxic gas sensors. Meanwhile, mesoporous spherical tin dioxide–graphene nanoparticles as formaldehyde gas sensors (Chen et al. 2016), copper oxide-y@ zinc oxide-α nanosized composites for improved room temperature nitrogen dioxide detection applications (Geng et al. 2017) and silver–iron oxide core–shell magnetic nanocomposite (Mirzaei et al. 2016) are the recent novel nano-sized composites that are used to fabricate sustainable toxic gas sensors. Similarly, photoluminescent carbon dots are synthesized with willow bark to fabricate gold nanoparticles-reduced graphene oxide nanocomposites, which is useful as a glucose sensor (Qin et al. 2013). Likewise, gold–chitosan nanocomposites as caffeic acid sensors (Di Carlo et al. 2012), silver nanoparticle-graphene oxide nanocomposite as tryptophan sensor (Li et al. 2013), palladium–gold–carbon dot nanocomposite to sense colitoxin DNA in human serum (Huang et al. 2017), graphene-nanosized gold particles hybrid as surface-enhanced Raman-scattering biosensor (Khalil et al. 2016) and nanosized flower-shaped reduced graphene oxide–iron oxide hybrid composites for sensing riboflavin (Madhuvilakku et al. 2017) are the novel nanocomposite-based sustainable biosensors that are under extensive research. Even though there are several nanomaterials that are synthesized using green and biosynthesis approaches, there exist certain limitations while using nanomaterials as sensors which have to be addressed before employing them for large-scale sensor applications.

5 Limitations and Future Perspective

The nanomaterial sensors are becoming an integral part of any sensor research due to their enormous applications (Luo et al. 2006). It is noteworthy that nanosensors are the hot topic in recent nanotechnology researches to develop enhanced sensors with rapid sensitivity and excellent detection limit (Ding et al. 2010). However, there exist several limitations to use nanomaterials in the fabrication of large-scale and commercial toxic gas and biosensors (Wang et al. 2013). Most of the commercial nanosized toxic gas and biosensors are fabricated via chemical approaches as shown in previous sections. These chemically synthesized nanomaterial-based sensors may lead to toxicity toward humans and other organisms (El-Safty et al. 2007). Moreover, it may accumulate as wastes over its lifetime and the toxic chemicals upon degradation may react with the environment (soil, air, or water) and lead to hazardous effects (Khin et al. 2012). This has led to the emergence of green and biosynthesis approaches to fabricate nanomaterials for sensor applications. These synthesis approaches have provided less or nontoxic nanomaterials for sensor fabrications (Zhang et al. 2012a). However, nanomaterials from green or biosynthesis are unstable most of the time and agglomerate to become micro-sized particles which alter their significant sensor properties (Wahab et al. 2018). Thus, it is highly essential to blend chemical, green, and biosynthesis approaches in the right proportion as a hybrid approach to fabricate sensors to avoid toxicity and improve stability with enhanced sensing properties. Moreover, the latest nanomaterials are focused on detecting a specific molecule, either gas or biomolecules, with enhanced detection limit and sensitivity (Yang et al. 2015). The future research of nanomaterial-based sensors must focus on multi-molecule detection, which can detect several toxic gases and biomolecules. This is highly possible by fabricating complex nanocomposites that can be tailored based on the requirement of sensors for desired applications.

The future of toxic gas and biosensors is based on their incorporation with wearable technologies and in biochips that can be implanted in the patients (Shafiee et al. 2018). Generally, nanomaterials are designed to either sense toxic gases or biomolecules (Smith et al. 2017). In future, multitasking nanomaterials will be designed to detect both toxic gas and biomolecules (Gu and Zhang 2018). These multitasking nanomaterial-based sensors will reduce the cost as well as the time and effort needed to produce such sensors (Casanova-Chafer and Llobet 2019). Moreover, these novel sensors will be incorporated into fabrics to sense toxic gases in the environment, inhalation or exposure level of toxic gas toward humans and detect biomolecules related to disease in patients (Hu et al. 2018; Jang et al. 2018). Recently, fabrics with sensors are available which possess sensors and can change color upon sensing toxic gas in the environment (He et al. 2019). Likewise, multitasking nanomaterial-based sensors can be incorporated in smartwatches and mobile phones to detect toxic gases as well as disease-related biomolecules (Tiwari et al. 2019). These smart technologies will serve as a display to know the level of detecting toxic gas or biomolecules and can be monitored by physicians (Tabatabaee et al. 2019). Such sensors will be the future of biomedical sciences which will reduce the burden of

Fig. 1 Summary of futuristic nanomaterial-based sensors for toxic gas and biosensor applications

patients and physicians in continuous monitoring of analytes. It will also help in the fabrication of fabrics that can monitor both toxic gases and biomolecules, which can help firefighters, workers in mines, and the people who work in extreme conditions. It is noteworthy that nanomaterials can be used to fabricate sensor substrate (Kumar et al. 2015b), bind with the analyte for enhancing the detection (Cardinal et al. 2017), transducer (Zaretski et al. 2016), signal processors (Lu et al. 2011), and as an individual sensing material (Wang et al. 2003). Thus, nanomaterials will replace the current sensor market and enhance its ability to be present in any tools that are used by consumers for sensing toxic gases and will be used as implantable biochips in the future that can sense disease and deliver drugs in the target site. Figure 1 is the summary of futuristic nanomaterial-based sensors in different toxic gas and biosensor applications.

6 Conclusion

This chapter is a summary of distinct nanomaterials that are used for the fabrication of toxic gas and biosensors. Metal, carbon, polymer-based nanomaterials, and nanocomposites are widely used in sensor fabrication applications. However, it was noteworthy that chemically synthesized nanomaterials are proved to be toxic toward humans as well as environment and are not suitable for implantable biosensors. Thus, green and biosynthesis are introduced to fabricate sustainable, nontoxic, and stable sensors to detect toxic gases and biomolecules. Biosynthesis using extracts from plants and bacteria as well as green synthesis using sunlight, ultraviolet, visible, and infrared radiation are used as catalyst and reducing agent to fabricate nanomaterials for sensor applications. However, there are several limitations to utilize green and biosynthesized nanomaterials for large-scale and commercial sensor applications. In future, it is possible to overcome these limitations with the advantages and swift progresses in nanotechnology field for the emergence of futuristic sensors. These futuristic sensors can be incorporated into fabrics, smartwatch, phones, paints, and several other tools that a consumer will use in their day-to-day life for toxic gases and biomolecules detection.

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