NANOSENSORS FOR DETECTION OF GASES AND HEAVY METALS

Abstract

Environmental monitoring is a crucial activity for protecting the public from dangerous substances released into the environment and for alerting them to their presence. Pollutants can be found in a variety of environmental media, including air, soil, and water. Hazardous gases from sources like automobile emissions, power plants, refineries, industrial and laboratory activities, as well as volatile organic compounds, such as sulphur dioxide, carbon monoxide, nitrogen dioxide, and sulphur dioxide, are examples of air pollutants. The synthesis, characteristics, and uses of materials with nanoscale dimensions are the focus of the newly growing scientific field known as nanoscience. Comparing the nanodimensional materials to their bulk equivalents reveals that they frequently exhibit completely unique characteristics and behaviours. The principal sources of heavy metal ions are natural and man-made substances. Due to its acknowledged accumulation and hazardous effects on the environment as well as biological media, it has grown to be one of the most significant societal challenges. To limit the hazards posed by environmental hazardous metal contaminants, important steps are needed. The utilization of technologies based on electrochemical detection in combination with tailored nanomaterials, as well as expanded research into heavy metal ions detection, is a crucially novel and promising approach that may be able to limit heavy metal poisoning. The application of Nanosensors for the detection of gases and heavy metals has been examined in this review.

Keywords: Nanomaterials; Nano adsorbents; Nano catalysts; Nanofilters; Nanosensor

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I. INTRODUCTION

Unintended emissions of gases, particles and aerosols into the inferior atmosphere are referred to as air pollution. [1]. such pollution is due to both sources viz; artificial and natural (such as wind-borne dust, volcanic eruptions, and forest fires). The gases and particles that pollute the air result in risk to human health. Nitrogen oxides, sulphur oxides, hydrogen sulfides, small powder particles (aerosols), and volatile organic compounds are the most common types of air contaminants (VOCs). According to the World Health Organization (WHO), lung cancer, chronic obstructive pulmonary disease, cardiovascular disease, stroke, and acute respiratory infections are among the seven million people who die each year from the combined effects of interior and outside air pollution. WHO data confirms that nine out of ten people breathe in air that exceeds WHO's guidelines for contaminant levels, with the highest exposures occurring in middle-income and low-income countries [2]. Additionally, the WHO is assisting a number of nations in combating air pollution. From urban smog to indoor smoke, there is a significant risk to health and climate. For the purpose of environmental protection from the adverse effects of pollution, a number of nations have enacted legislation regulating numerous pollution groups and justifying their adverse effects. At the nanoscale use of science, engineering, and technology, which ranges from one to one hundred nanometers, is known as nanotechnology. In general, nanotechnology, which often refers to structures with dimensions of 100 nm or less, involves the creation of substances and devices that fit inside this size range. Nanotechnology is incredibly diverse, ranging from completely new methods based on molecular self-assembly for the creation of nanoscale-sized sophisticated materials to the development of nanoscale-sized advanced materials. It is also feasible to directly influence matter using nanotechnology at the atomic level.

The current chapter involves the use of several nanomaterials in the remediation of contamination of air. The current study involves the investigation of nanomaterials in the sense of Nanosensors. Various nanostructures, including nanoparticles, nanofibers, nanorods, nanosheets, and nanowires, have been stated for use in air purification. We primarily investigate materials based on carbon and metal-based nanomaterials for the removal of airborne contaminants. In conclusion, the potential environmental effects of nanomaterials (metal-based nanomaterials and carbon-based nanomaterials) are discussed.

Nanosensors: Currently, Nanosensors are generated by various nanomaterials with piezoelectric, thermal, optical, and electrochemical properties that react quickly and can detect chemicals in very small amounts (as low as 1 ppb) [3]. Graphene, carbon nanotubes, metal, and metal-oxide-based nanoparticles are examples of nanomaterials used in sensor applications. These nanoparticles are tailored for sensing and measuring various air contaminants, such as toxic gases (e.g., NO_2, H_2S, and SO_2) and heavy metal ions. In the sections that follow, various nanotechnology applications for the detection of toxic gases such as NO_2, H_2S, and SO_2 are discussed.

II. DETECTION OF TOXIC GASES AND GREENHOUSE GASES

1. **Detection of Nitrogen Dioxide (NO_2):** Nitrogen dioxide is a prevalent air pollutant that is primarily observed as a mixture of nitrogen oxides (NOx) in varying proportions (x). This gas is toxic, irritant, and reddish-brown in color, with a distinct pungent and stinging odor. Because graphene-based materials are stable physically and chemically owing to

more surface area, and better carrier mobility at room temperature, they are good options for the development of room-temperature gas sensors. [4, 5]. A potential method for obtaining high-performance r-GO-based sensing materials is to modify the surface of r-GO using covalent or non-covalent techniques to alter its semiconductor properties. r-GO-multiwalled CNTs–tin oxide nanoparticles hybrids, made graphene oxide (GO)-multiwalled CNT dispersion treatment hydrothermally with tin tetrachloride [6], were used as sensing materials to make a better NO_2 Nanosensor. The recovery rate of r-GO-multiwalled CNTs–tin oxide nanoparticles hybrids is good, having a fast response, better selectivity and stability at RT to find nitrogen dioxide. This made it better than other r-GO-based NO_2 sensors that had been reported.

Agarwal et al. [7] informed an effective and flexible chemoreceptor-type nitrogen dioxide gas sensor made from CNTs with a single wall on PTFE membrane filter substrates. This sensor is created by using a cost-effective spray coating to prepare a thin film of single-walled carbon nanotubes, then, by shadow mask and polyethyleneimine usage, the single-walled carbon nanotubes were made to have noncovalent properties. Compared to ammonia, this was more sensitive to nitrogen dioxide gas at room temperature and dry air, 167.7–21.58 % for amounts of 5–0.75 mg/l. Ammonia was insensitive. Wang et al. [8] made an r-GO hybrid material with molybdenum disulfide nanoparticles for a two-stage wet-chemical method to detect nitrogen dioxide. CNT–based gas sensors in contrast to conventional metal oxide–based semiconductor gas sensors offer several advantages, including higher sensitivity, lower operating temperature, and lower power consumption [9,10] developed selective and ultrasensitive gas sensors based on solution-processed single-wall CNT random networks for room-temperature detection of nitric oxide down to parts per billion. These sensors demonstrated a 50% response in both air and inert atmospheres, with a detection limit of 0.20 ppb and a selectivity toward various contaminant gases of volatile organic compounds, including ammonia, toluene, and benzene. By using ultraviolet light to get photo desorption energy, the recapture time of these cutting-edge N_2O gas monitors was cut down to a few tens of seconds. Furthermore, silicon ox carbonitride functionalization is suggested for improved reliability, reproducibility, and stability in CNT-based gas sensors [11]. Following heat treatment, a thin film of the semiconducting ceramic silicon ox carbonitride is formed on the CNTs. This method is extremely straightforward, as the liquid precursor completely coats the CNT surfaces without requiring surface modifications. This advanced conductometric gas sensor can detect up to 10 ppm of ammonia and 2 ppm of nitrogen dioxide at temperatures as high as 350^0 C.

2. **Detection of Hydrogen Sulfide (H_2S):** As little as 100 parts per million, H2S is an irritating and dangerous gas. Gas monitors that are very selective and sensitive can help protect people and the environment from gases that are flammable but don't smell. Numerous metal oxide-based sensors have been used to find H_2S, but zinc oxide is thought to be the best gas-sensing material as it has great properties, like being chemically stable, non-toxic, and easy to make into nanosheets, nanorods, nanocrystalline structures, and nanowires. [12,13] used a simple colloidal technique with oleic acid as a surface-capping ligand to make colloidal ZnO quantum dots. CQDs are becoming good options for gas sensors because they are easy to process, inexpensive, and easy to integrate. For the development of chemo-resistive gas monitors, zinc oxide CQDs were spin-coated on ceramic substrates after being properly spread out. The long-chain surface

capping was taken off with a film-level ligand-exchange process, which made it easier for both gas adsorption and carrier transport. The best sensor had a reaction time of 16 seconds and a response value of 113.5 when exposed to 50 mg/l of hydrogen sulfide at RT. The results showed that zinc oxide CQDs could work as high-performance gas monitors. Nanocomposites made of metal oxide and graphene are starting to look like good options for making high-performance gas monitors. Song and others [14]. Scientists have shown that tin(IV) oxide quantum wires attached to r-GO nanosheets at room temperature can be used to make sensitive H_2S gas monitors. Tin (IV) oxide morphology-related quantum confinement has been managed by altering the time of reaction in a single-step colloidal preparation method owing to r-GO steric hindrance effect. Tin (IV) oxide quantum wire/r-GO nanocomposites were spin-coated without any sintering on ceramic substrates for the development of chemi- resistive gas sensors. The optimal sensor response to 50 ppm H_2S is 33 in two seconds and is completely reversible upon H_2S release at 22 degrees Celsius. These sensors are extremely advantageous for the ultrasensitive detection of H_2S gas with reduced power consumption due to their easy fabrication and operation at room temperature. Shanmugasundaram et al. [15] made a system of tiers. Mesoporous nickel oxide and boron-nitrogen co-doped r-GO composites was employed to detect H_2S.

The boron–nitrogen co-doped r-GO nanodisk composite sensor's reaction to 100 mg/l H_2S at 150 C was almost 82, and the sensor could detect about 24 ppb. Also, the sensor's answers were twice as strong as those of r-GO sensors with nickel oxide and three times as strong as those of nickel oxide nanodisk sensors. This composite is perfect for possible real-world applications, especially in explosive environments and in medical diagnosis, because it is easy to make, has high stability, responds quickly, is selective, and works at room temperature.

3. **Detection of Sulphur Dioxide (SO_2):** SO_2 is considered to be the primary pollutant in vehicle exhaust, thermal power plant emissions, and chemical production processes [16]. Also, SO_2 gas is a pollutant of the atmosphere and a dangerous gas. People can only handle about 5 ppm of it, which can cause serious diseases like lung cancer, heart disease, and respiratory disease. Using a first-principles method based on spin-polarized density functional theory, Shao et al. [17] revealed that intrinsic graphene should not be reflected as an active component for SO_2 absorption. Ren et al. [18] fabricated an SO2 gas sensor with chemical vapor deposition-grown graphene configured in a field effect transistor device and demonstrated its detection properties at a concentration of 50 ppm SO_2. Zhang et al. [19] verified the ultralow SO_2 gas sensing capabilities of a self-assembled TiO_2/graphene film device at room temperature. The developed film was produced by the alternate deposition of TiO_2 nanospheres and GO to form a nanostructure, followed by the reduction of GO into r-GO. At RT, lower amounts of SO2 gas were used to test how well the TiO2/r-GO hybrid could sense gases. This SO2 gas sensor could identify SO2 at ppb levels, had good reversibility, responded and recovered quickly, was selective, and could be used over and over again. This sensor's potential sensing mechanism was due to the synergistic effect of TiO_2 and r-GO, as well as the unique interaction at titanium dioxide/r-GO interfaces. The formulated TiO2/r-GO film sensor could be used to detect SO2 because it has better sensing skills, uses less power, and is cheap. Liu et al. [20] made zinc oxide nanosheets with ruthenium/alumina catalysts

on them and put them in a microsensor that can detect SO_2 gas. Petryshak et al. [21] show the spectral properties of cholesteric–nematic under the SO_2 effect, single-walled CNTs, double-walled CNTs, and multi-walled CNTs were mixed in with the rest of the material. Thus, the sensitivity of the composite changes based on how it is made and the highest spectral sensitivity coefficient is seen at 0.30 percent nanotube concentration.

4. **Heavy Metal Detection and Removal:** Most of the time, nanoparticles are used as adsorbents to remove heavy metals. NMTs, viz; zero-valent iron, magnetite, graphene, and carbon nanotubes, have distinctive qualities, such as high surface-to-volume ratio, stability, inertness, reactivity, and biocompatibility which proves it to be a good possibility for adsorption. Heavy metals, for instance organic substances, don't break down. They build up in food chains and hurt both people and animals. [22,23]. In the last few years, nanoparticles made from iron have become the best way to get rid of heavy metals in water. Zero-valent iron is often used for adsorption of Pb^{2+} (lead), Ni^{2+} (nickel), Zn^{2+} (zinc), Cd^{2+} (cadmium), Cr^{+6} (chromium), and Cu^{2+} (copper) because it is strong, easy to make, and has a feature that makes it reduce. Nano-zero valent iron (nZVI) was used by Azzam et al. [24] to get Pb (II), Ni (II), Cu (II), and Cd(II) ions out of a water solution. Maximum adsorption capacity (max) was found to be in the following order: Pb^{2+} has 1666 mg/g, Cu^{2+} has 181 mg/g, Cd^{2+} has 151 mg/g, and Ni^{2+} has 133 mg/g. The metal ions were physically attracted to the surface of nZVI at first, and then that the metal ions and nZVI together precipitated. Metal ions are mostly removed at a rate that depends on the pH of the solution. This suggests that surface generation of nZVI enhanced the rate of adsorption. Heavy metal remediation also involved important mechanisms viz; reduction. In their review, Fu et al. [25] defined the reactions involved in chromium reduction. The hexavalent form of chromium (Cr+6) was found to be a harmful pollutant in the environment, so it needs to be changed to the nontoxic form (Cr^{+3}). Through the movement of electrons, the iron particles become Fe^{+3} ions and the hexavalent chromium becomes Cr^{+3} (Equations 4.1 and 4.2). Iron and chromium are subsequently precipitated as Fe and Cr hydroxides. However, because nZVI is magnetic, it tends to stick together, which makes the nanoparticles less active. This problem is resolved by immobilizing nanomaterials on a substrate, which may be composed of polymer, metal, or porous material.

$$Cr2O2^{-7} + 2Fe + 14H^{++} \rightarrow 2Cr3+ + 2Fe3+ + 7H2O \quad (4.1)$$
$$Cr^{3+} + Fe^{3+} + 6OH \text{ yields } Cr(OH)3 \text{ and } Fe(OH)3 \quad (4.2)$$

Heavy metals can also be removed with other magnetic particles, such as Fe_3O_4. Shi *et al*. [26] synthesized Fe3O4 nanoparticles via a green synthesis technique employing flavonoid polymer complex proanthocyanidins (PAC) and used them for the adsorption of Pb2+, Cu2+, and Cd2+ from water. The highest removal rates for Cu^{2+}, Cd^{2+}, and Pb^{2+} were 96%, 91%, and 87%, respectively. According to their study, the hydroxyl ions in PAC coordinate with metal ions and form a complex with Fe-PAC, which speeds up the adsorption. Lin et al. [27] treated As (V), As (III), and Cr (VI) with magnetic iron oxide nanoparticles (Fe_3O_4 and -Fe_2O_3) in a system where they were all present at the same time. The removal process is caused by the formation of a sphere made of hydroxyl ions on the outside and a sphere made of metal ions on the inside. As(V) has a bigger binding energy than As^{3+} (0.35 eV) and Cr^{+6} (0.26 eV), it pushes As (III) and Cr (VI) out of the outer sphere of iron oxide nanoparticles. This makes iron oxide nanoparticles very attracted to As (V) ions. At higher pH values, more nanoparticles were needed to get rid of extra metal ions Cr (VI) and As(III)). Nanofiber membrane filtering was also used to deal with metal ions. Liu et al. [28] used nanofibrous composite membranes modified with polyacrylonitrile (PAN) and polyvinyl alcohol to remove chromium and cadmium from polluted water (PVA). Because the PAN-modified membrane has amino groups on its surface, it can hold more Cr^{+6} (66 mg/g) and Cd^{+2} (33 mg/g). Nanomaterials act as catalysts in different ways that things break down. Heavy metals that don't break down, like arsenic, chromium, cadmium, lead, mercury, zinc, and nickel, are thought to be harmful to the environment. So, they build up in nature and can get into the body, where they can cause kidney damage, stomach pain, high blood pressure, indigestion, nausea, headaches, and even lung and nose cancer. Metal ions and metals may be removed by many means, viz; physical binding [29,30], ion exchange, electrostatic interaction, and hard/soft acid-base interaction [31]. Nanoadsorbents that can be used to remove heavy metals include those made of carbon, polymers, magnetic or nonmagnetic materials, biopolymers, metal oxides, and zeolites. Carbon-based nanomaterials are good at removing heavy metal ions because they have a large specific surface area, are easy to change chemically or physically, and can hold a lot of ions. CNTs have many active adsorption sites on their surface, internal channels, and intermediate channels, sites, and grooves on the outside [32]. Physical or chemical changes can be made to carbon nanotubes (CNTs) to make them better absorbents. [33]. Hayati et al. [34] took Cu^{2+} and Pb^{2+} out of a water solution by adding four generations of poly-amidoamine dendrimer (PAMAM, G4) to CNT. They concluded that PAMAM/CNT nanocomposites are super-absorbent and can take in a lot of heavy metals from liquids with a single or binary component. Researchers made a CNT hybrid by putting fullerene CNT and zinc ferrite ($ZnFe_2O_4$) together. They did this to expand the ability of fullerene CNT to absorb things. They established crushing fullerene CNTs with a $ZnFe_2O_4$ combination made the free fullerene CNTs better at absorbing Hg (II), Pb (II), and Cd (II) by 25%., Elsehly et al. [35] made CNT-based filters by modifying CNT with ion-beam irradiation. The high disorder in the irradiated samples led to an increase in Mn (II) removal rate of up to 97.5% in the filters. It was found that using biopolymers to remove heavy metals is effective, good for the earth, and cheap. Charpentier et al. [36] employed magnetic carboxymethyl chitosan nanoparticles to attract heavy metal ions. Accordingly, the nanoparticles' magnetic qualities made it easier for heavy metal ions to stick to them.

III. FUTURE SCOPE OF NANOSENSORS

It is clear even from this small sample size that nanosensing technologies have advanced significantly since they were first discussed in this journal. Even though the technology is still in its infancy, more and more innovations are getting to the point where commercialization is just around the corner. What we are currently witnessing is only the beginning; when new materials and production techniques are created and fresh nanoscale phenomena are identified, a wide variety of unique sensors will emerge. Additionally, the combination of nanomaterial characteristics with nanotechnology creates a significant opportunity for the growth of extremely highly integrated recognition organizations, allowing for the development of dedicated online or even embedded heavy metal detectors that are relevant to environmental revisions and other related fields. Advanced miniaturized techniques might pave the way for multiplexed, quick, cheap, easy, and economical HMI detection.

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