







Review Article

Sensing Techniques on Determination of Chlorine Gas and Free Chlorine in Water

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Chlorine gas is a greenish-yellow gas that is one of the most utilized gases in numerous industrial fields. It has been categorized as a choking agent that can threaten human, animal, and environmental safety. Currently, development of highly sensitive, selective, and precise chlorine sensors receives much attention. This review focuses on several sensing techniques used for chlorine gas and free chlorine in water. The fundamental working principles, as well as the sensing mechanisms of chlorine detection covering spectrophotometric, electrochemical, and optical techniques, are described. A comparison of various sensing materials is also discussed. Finally, an overview of the future improvements needed of high-performance chlorine sensors was suggested.

1. Introduction

Chlorine was first produced by Carl Wilhelm Scheele in 1774 and described in a paper he authored on manganese. It was investigated by Humphrey Davy in 1807, and he eventually concluded that it was an element. Commonly, Cl₂ has been used as a disinfecting agent in our daily activities because of its low cost and efficiency in maintaining a clean, hygienic area over fairly long period of time. However,

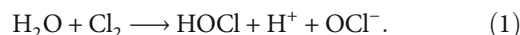
excess chlorination when maintaining hygiene is wasteful and may cause a worsening of aesthetic qualities, produce dangerous side effects, and can intensify corrosion effects on materials exposed to it which than can lead to consumer complaints [1]. There are numerous sensing materials used to detect chlorine gas. One of the popular demands is utilization of metal oxide [2]. Semiconductor metal oxide sensors such as SnO₂, ZnO₂, and WO₃ have frequently been used as gas sensors [3–8]; nevertheless, they do require significant

power consumption because of their need to operate at high elevated temperatures and generally also have selectivity issues. Hence, there is a continuing need for novel gas sensor material to be developed. Apart from magnetic and electrical applications, ferrites are being studied for gas and humidity sensing applications [9–12]. Ferrite nanoparticles have been reported as useful gas sensors for different gases such as CO, H₂S, and Cl₂ and for liquefied petroleum gas (LPG) [11, 13–16]; however, ferrite thin films as gas sensors have received less attention. Thin film sensors provide certain advantages, which include a high surface area to volume ratio, which improves the interaction between the gas analyte and the sensing material, lower energy input, low power consumption, compactness, and overall cost efficiency [17]. Consequently, the sensitivity and selectivity of gas sensors using this material will be enhanced. Aside from that, as shown in Figure 1, a search on <http://lens.org> using the keyword “metal oxides-based gas sensor” revealed that the number of publications focusing on metal oxides as sensing material has increased in recent years. Therefore, this demonstrates that research on metal oxides as gas sensors continues to pique the interest of scientists in this decade.

A metal oxide sensing mechanism is mostly dependent on charge transfer mechanisms, which include oxygen and target analytes [18]. When the sensing material is operated at temperatures above 150°C, oxygen molecules from the air chemisorb onto the sensing material’s surface, thus capturing electrons and transforming them into O₂⁻, O⁻, or O²⁻, whereas when the sensing material is operated at room temperature, the opposite trend occurs. As an electrical charge carrier, the majority carrier is hole, and the target analyte will chemisorb onto the sensing material’s surface, reducing the concentration of holes and thereby increasing the sensing material’s resistivity [19]. Available papers that report the efficient gas sensing performance of ferrite nanoparticles are listed in Table 1.

According to the Occupational Safety and Health Administration (OSHA), the exposure limit of Cl₂ for human beings is 1 ppm for the short-term exposure limit (STEL) and 0.5 ppm for its time-weighted average (TWA). It has an odour threshold of approximately 0.3–0.5 ppm, which means that humans are able to identify the pungent odour at this relatively low level. Cl₂ gas when inhaled into the respiratory tract at concentrations above 30 ppm begins to react with water, which then changes it into hydrochloric acid (HCl) and hypochlorous acid (HOCl) (equation (1)) [25]. These acids in the respiratory tract will cause symptoms such as cough, dyspnoea, and retrosternal chest pain [26, 27]. At concentrations greater than 50 ppm, these acids will cause cellular damage to the lung parenchyma and bronchial tree, whereupon this damage will result in the clinical features of pneumonitis and pulmonary oedema. Exposure to higher concentrations of Cl₂ gas (from 60 ppm) will lead to irreversible lung damage, while exposure to even higher concentrations such as 430 ppm for 30 min will lead to life-threatening effects (Figure 2). When exposed to even higher concentrations such as when the concentration exceeds 1000 ppm, death may occur within a minute of the exposure [28, 29]. Thus, the threshold level of Cl₂ gas detec-

tion is applied at 0.5 ppm for human health and environmental safety.



Plants and animals are unlikely to accumulate Cl₂ in their systems, but laboratory tests have shown that repeated exposure to Cl₂ in the air can affect the blood, immune system, heart, and respiratory systems of animals while causing bleaching of chlorophyll and of flowers in plants. There seems to be minimal effects of Cl₂ exposure to the environment, but it is known to cause greater harm towards organisms living in water and soil [30]. Furthermore, unintentional releases of high concentrations of Cl₂ gas can cause depletion of the ozone layer, cause acid rain showers, and contribute to global warming [21].

Besides these environmental effects, Cl₂ has also been misused as a chemical weapon. It has the distinction of being the first chemical used as an offensive weapon in conventional warfare in World War I in the Second Battle of Ypres, Belgium, on 22 April 1915. Here, chlorine gas from cylindrical tanks in the German frontline were released on the battlefield and allowed to be carried by the wind to the trenches of French, British, and Canadian soldiers resulting in numerous casualties and deaths from inhalation of the gas [28]. This use led chlorine to be identified as a chemical warfare agent (CWA) in the class of choking agents. Typically, CWAs are extremely toxic chemicals, which may be synthetic, that can be dispersed as a gas, liquid, or aerosol or as agents adsorbed onto particles so as to become a powder for dispersal [31]. There are about 70 different chemicals that have been used or stockpiled as CWAs since the 20th century. These CWAs are commonly categorized according to their mechanism of toxicity in humans into various classes, namely: pulmonary agents, blood agents, nerve agents, blister agents, and choking agents [32]. Cl₂ is classified as a choking agent because inhalation of Cl₂ gas can cause cellular pulmonary damage that can result in pneumonitis and pulmonary oedema. It will cause reduced pulmonary compliance and result in altered gas exchange, which is a result of the inflammatory reaction occurring in the pulmonary tract and lungs [33]. After long-term exposure, it can result in tracheobronchitis, adult respiratory distress syndrome (ARDS), and temporary airflow dysfunction which is described as “Reactive Airway Dysfunction Syndrome” (RADS) [34]. RADS is the result of inhalation of high concentrations of highly irritating substances such as ammonia, chlorine, and sulphuric acid. The symptoms of RADS are described as asthma-like symptoms and include wheezing, difficulty in breathing (dyspnoea), cough, and a sensation of chest tightness. These symptoms typically appear 24 hours after the inhalation occurs and may remain for at least three months after the exposure [35]. The pulmonary damage after exposure to gases with a corrosive action can result in permanent cellular damage leading to fibrosis of the lungs and a diminished gas exchange capacity that may lead to chronic conditions such as Chronic Obstructive Pulmonary Disease (COPD) which has permanent consequences and is irreversible.

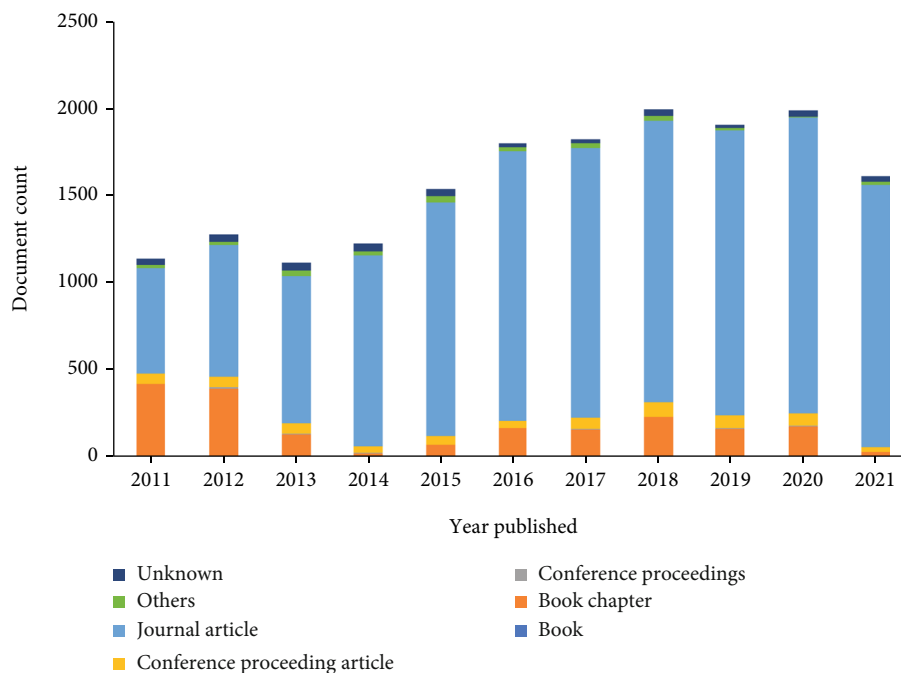


FIGURE 1: Bar chart of published manuscripts focusing on a metal oxide-based gas sensor.

TABLE 1: Reports on the efficient gas sensing performance.

Material	Operating T ($^{\circ}\text{C}$)	Gas	Sensitivity	Ref.
Ag-modified bismuth ferrite	240	Cl_2	72.62	[16]
Magnesium ferrite	200	H_2S	Response time: 18 s Recovery time: 108 s	[20]
NiFe_2O_4 and Pd: NiFe_2O_4	325	Cl_2	0.9	[21]
Mn-doped Ni-Zn ferrite	100	Cl_2	115-212%	[22]
Zn-substituted cobalt ferrite	30	$\text{C}_2\text{H}_5\text{OH}$	34	[23]
Bi-Co ferrite	230	NO_2	34	[24]

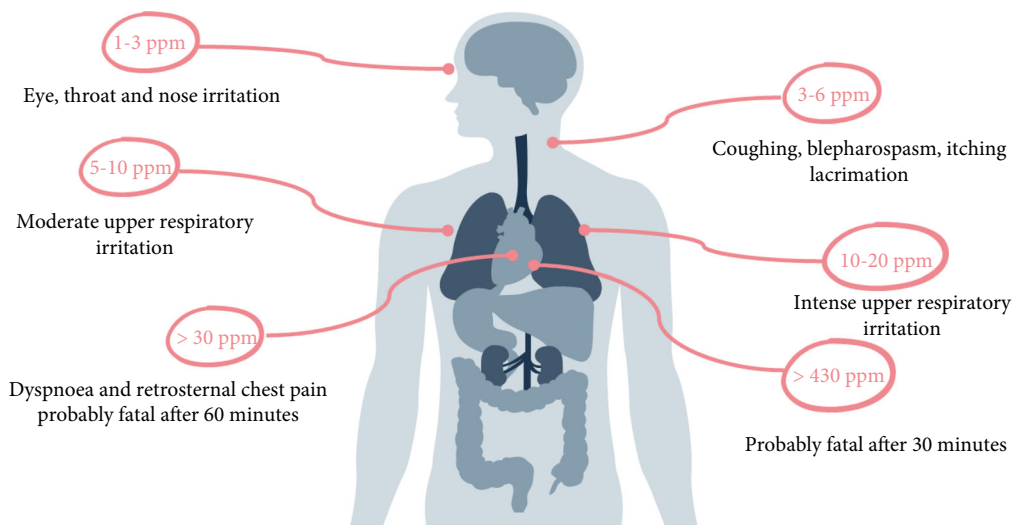


FIGURE 2: Toxicity of chlorine gas.

Therefore, the detection of Cl_2 is a matter of very serious concern in order to prevent unnecessary incidents and avoid exposure to dangerous concentrations of the gas since this can lead to the occurrence of lethal events resulting from overexposure to chlorine gas to humans as well as to the environment caused by a release of Cl_2 into the environment. The use of Cl_2 as a chemical weapon is also a matter of serious concern as it is a gas commonly available in various industries and in the treatment of water. Such a sensor is a device that can be categorized into two main categories, i.e., natural, and man-made sensors. The mechanism of operation of natural sensors is a situation where a stimulus signal is processed and then transferred as an electrochemical signal, typically created by ion exchange, and can be found in many living things. In the case of man-made sensors, the stimulus signal is transmitted and processed in the form of an electrical signal caused by charge exchange (specifically within electron transport mechanisms) [36].

It is a matter of importance that with the ubiquitous use of Cl_2 in many industries and its relative public availability, the risks of Cl_2 exposure remain a major concern. Thus, improvements in Cl_2 sensor performance are an ongoing need as many areas that require the use of or presence of Cl_2 would also need efficient Cl_2 sensors to monitor the risks of inadvertent or even deliberate exposure. Nanostructured materials could be a promising candidate as sensing material due to their high surface area, good sensitivity, quick response and recovery phase, and many more [37]. The binary metal oxide also could give good solution in production of a room temperature gas sensor. Furthermore, low detection level can be attributed to the coexistence of 3D structures based on hexagonal platelet-like and porous flower-like shape [38, 39]. It would be the foundation in the development of a room temperature gas sensor [40]. Figure 3 illustrates the various characteristics needed in the production of a good chlorine sensor. For better understanding, a brief description of the important major characteristics of a gas sensor is as follows [41]:

- (a) Sensitivity is the ability of the sensor to be able to detect a minimum concentration of the gas
- (b) Selectivity is the capability of the sensor to distinguish a specific gas from among a gas mixture
- (c) Stability is how stable the device is when operating under extreme conditions such as high ambient temperatures and high environmental pressures or in high-radiation or corrosive environments
- (d) Reproducibility is the ability of the sensor to correctly and consistently detect the gas after multiple exposures
- (e) Recovery is the ability of the sensor to regain its initial state after reacting with the target gas and being able to detect the next gas exposure

Numerous detection techniques will be considered in order to meet the critical performance criteria needed of a particular sensor, and the object would be to enhance the

sensing performance of the sensor in its working environment. However, it is known that it will be difficult to satisfy all the needed performance criteria when designing an ideal gas sensor. Thus, identifying the limitations of the working environment and the operational needs of the users is critical to understanding the compromises needed between the characteristics and performance of the gas sensor at the design level of development.

This review will begin with a description of the production and application of chlorine gas. Then, the working principles and sensing mechanisms of the most established chlorine sensing techniques will be discussed. Subsequently, recent progress in chlorine detection techniques will be deliberated, and this review will be concluded with a discussion of future trends in the advancement of innovative chlorine detection methods.

2. Properties, Production, and Applications of Chlorine

2.1. Properties of Chlorine. Chlorine can be categorized as a simple halogen pulmonary irritant (HPI) which is diatomic (Cl_2), and it is a volatile molecule that occurs in two stable isotopes, namely, chlorine-35 (75.53%) and chlorine-37 (24.47%). However, chlorine-36 is also known naturally and is a radioactive isotope with a half-life of about 30,000 years. Sodium chloride (NaCl), often known as crystalline rock salt, is a crystal lattice in which ions are linked together by electrostatic interaction, resulting in a more energetically favourable configuration of sodium and chlorine than the component elements individually. Ionic salts have a lower energetic configuration than their components, and the reactions that occur during the formation of ionic salts generate energy (see the equation below).



The release of 404 kJ energy indicates that sodium chloride formation is exothermic. As a result of the second law of thermodynamics, the released energy spreads out into the environment and is thus unavailable to drive the reverse reaction. Hence, sodium chloride is more stable than its component elements due to its irreversibility. In seawater, about 2% of its concentration comprises sodium chloride. Besides sodium chloride, other examples of chlorine-containing minerals include sylvite or potassium chloride (KCl), carnallite ($\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$), bischofite ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$), and kainite ($\text{KCl}\cdot\text{MgSO}_4\cdot 3\text{H}_2\text{O}$). These are found in evaporite minerals such as chlorapatite and sodalite. Table 2 shows the numerical properties of chlorine compounds.

2.2. Production of Chlorine. There are several methods of producing Cl_2 gas. It can be produced through the electrolysis of a NaCl solution, using a diaphragm cell [42–44] and a membrane cell. The electrolyzing process of NaCl creates three important substances, which are Cl_2 , hydrogen, and sodium hydroxide [45]. NaCl presents in the form of underground deposits of high purity. It is pumped to the surface with high-pressure water as a concentrated solution which

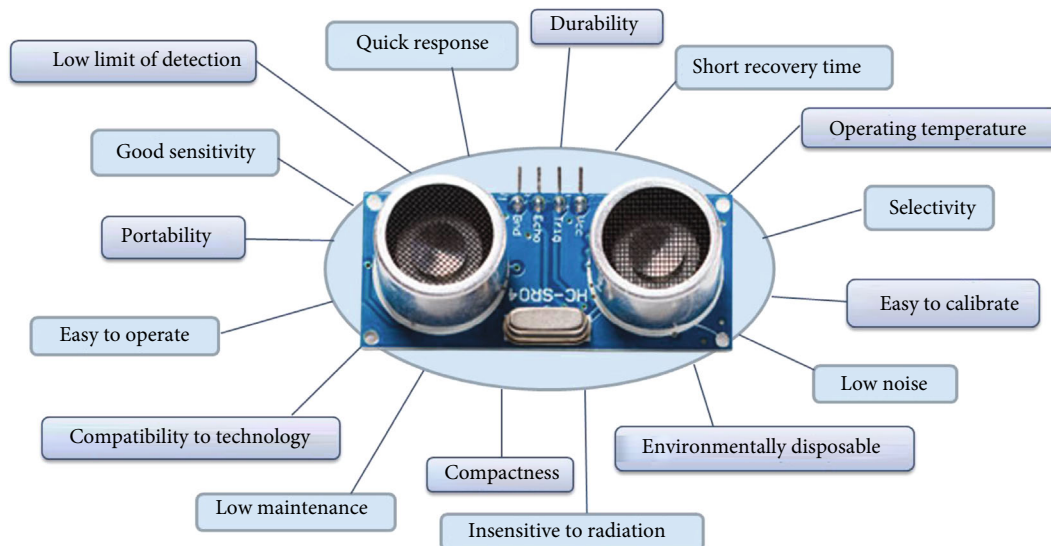
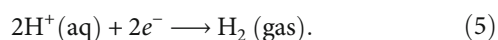
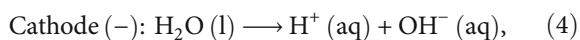
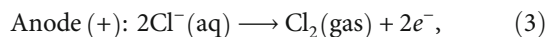


FIGURE 3: Characteristics of a good sensor.

TABLE 2: The numerical properties of chlorine (<http://www.environmentalpollution.in/water-pollution/chlorine-numerical-properties-hydrolysis-and-role/1774>).

No.	Properties	Value
1	Atomic number	17
2	Outer electron configuration	$3s^23p^5$
3	Molecular formula	Cl_2
4	Atomic weight	34.457
5	Stable isotopes, mass number	35.37
6	Oxidation states	+1 to +7
7	Melting point ($^{\circ}C$)	-102
8	Boiling point ($^{\circ}C$)	-34.6
9	Critical pressure (atom)	76.1
10	Density of solid (g/mL)	1.9
11	Electron affinity (eV)	3.75

is often called brine. A solution of sodium chloride contains Na^+ (aq) and Cl^- (aq) ions and, from the dissociation of water, very low concentrations of H^+ (aq) and OH^- (aq) ions. During the electrolysis of the solution, Cl_2 and H_2 gases are produced (see the equations below):



As the hydrogen is discharged, more water molecules dissociate to form extra H^+ and OH^- ions leading to an increase in the amount of OH^- ions at the cathode, thus producing NaOH solution. The main problem from the formation of this extra NaOH is that it could lead to the production of sodium hypochlorite (NaOCl) which can then react with chlorine. Therefore, most production plants are

known to now use ion exchange membranes [46] as a better method of chlorine production without depending on fossil feedstock [47]; thus, this would be more economically and environmentally friendly compared to the earlier processes.

An ion exchange membrane (Figure 4) is permeable to ions of one charge (counterions) and is impermeable to ions of opposite charges (coions), and they are used under conditions of hydrodynamic water flow [47]. In Cl_2 production, Na^+ ions can pass through in a hydrated form. Thus, some water is transferred too, but the membrane is impermeable to free water molecules [48]. To ensure the passage of desirable components in the production of Cl_2 , the ion exchange membrane must fulfil certain characteristics such as having high perm-selectivity and low electrical resistance and having good mechanical strength and stability as well as high chemical stability to operate in pH ranges from 1 to 14 and in the presence of oxidizing agents [49]. There are few other methods to produce chlorine such as by electrolysis of fused sodium chloride, where the yield is metallic sodium and chlorine evolves at the anode, by electrolysis of fused magnesium chloride, which produces metallic magnesium and chlorine as its by-products, and in the laboratory, chlorine is prepared using the oxidation of concentrated hydrochloric acid with the presence of permanganate or dichromate salts.

2.3. Applications of Chlorine. In water purification processes, Cl_2 is dissolved in the water as a disinfecting agent to prevent bacterial contamination of the water [51–53]. Cl_2 is commonly used as a sterilising reagent in various fields such as in healthcare, drinking water, and swimming pool and for sewage treatment [29, 54, 55]. In chemical industries, chlorine gas (Cl_2) is widely used as an industrial reagent in the manufacture of many products as presented in Figure 5, such as isocyanate epoxy resins, chloromethane compounds, silicone, polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC), herbicide, pesticide, gasoline additives, antifreeze

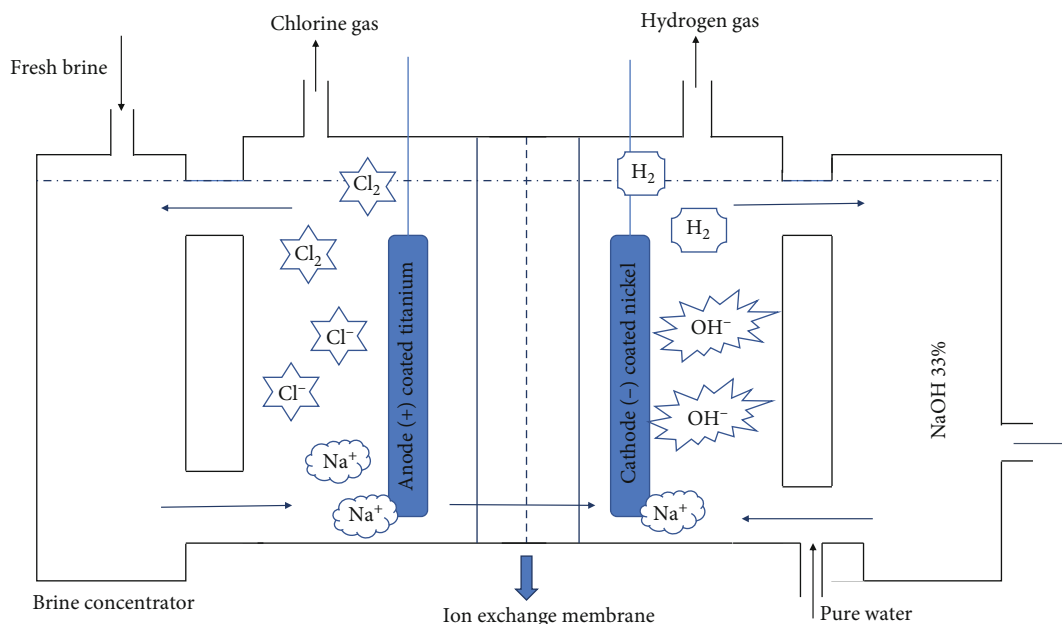


FIGURE 4: An ion exchange membrane cell [50].

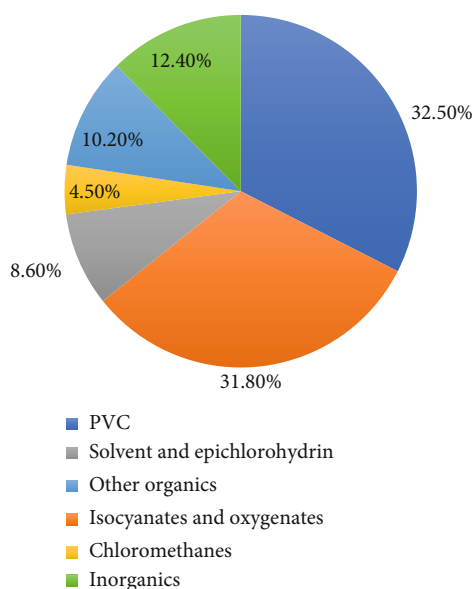


FIGURE 5: Chlorine gas applications [67].

compounds, and brake fluids, as well as in the production of prevalent metals such as magnesium (Mg), aluminium (Al), and platinum (Pt) in aeronautic industries [56, 57]. Beyond that, Cl_2 is also used in electronic industries for the production of computer components and microprocessors [29], high-performance magnets [58], wire and insulation cables [59], residential and commercial air conditioning refrigerants [60], nuclear batteries, and hybrid car batteries [61, 62]. The defence and security (law enforcement) industry also uses Cl_2 in various manufacturing processes to fabricate bullet-resistant vests worn by military and police officers [63]. They also use Cl_2 chemistry in improving parachutes and night

vision devices as well as in missile guidance technologies and cockpit canopy materials. In the medical field, almost 95% of pharmaceutical products utilize a variety of chlorine compounds for medicaments used to treat various diseases such as cancer [64], chronic periodontitis [65], diabetes [66], and many others.

3. Chlorine Sensing Techniques

Chlorine with lethal concentration in the atmosphere of 2.5 mg L^{-1} is a harmful substance. Inhaling chlorine gas or drinking extremely concentrated chlorine sources (such as domestic bleach) can cause vomiting, unconsciousness, and even death [68, 69]. Therefore, sensitive, reliable, durable, and inexpensive sensors would be invaluable for real-time monitoring of Cl_2 concentration in the air in a wide range of industrial environments. Till today, many analytical methods using various sensing principles have been reported and developed, and these are depicted in Figure 6. These methods are described individually in Figure 6.

In this part, we will look at two different types of chlorine. Chlorine is basically of two types: gaseous and aqueous. The type of sensing mechanism will be determined by the distance in chlorine form. Chlorine in gaseous form, for example, will adsorb on the surface of the sensing material. When exposed to chlorine gas, the sensing material will produce signal outputs such as resistance, conductance, or color changes. Chlorine gas is a strong oxidizing gas. It tends to accept electrons from sensing materials and, depending on the type of sensing material, leads to changes in the concentration of hole/electron carriers. Working temperature, dopants of sensing material, type of material used (such as metal oxide, polymer, nanoparticle, or carbon material), humidity, functionalization with other compounds, and other factors

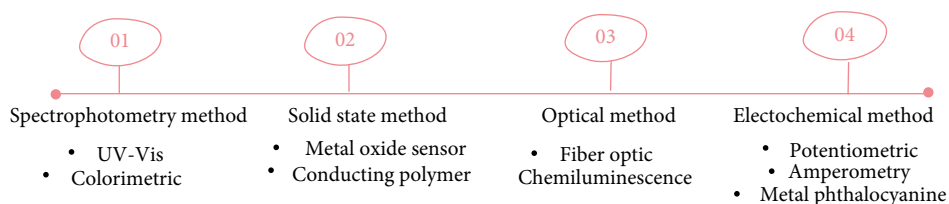


FIGURE 6: Types of chlorine gas sensors.

can all affect the sensitivity and response of the sensing material. All of these criteria have the potential to improve the performance of sensing materials and provide a great potential for use in low- or high-concentration chlorine detection.

On the other hand, free chlorine in water will involve pH value, where chlorine gas will convert to hypochlorous acid (HOCl) or hypochlorite ion (ClO^-). The most common chromophores for photometric and visual detection of free chlorine are N,N-diethyl-p-phenylene-diamine (DPD) and syringaldazine (SA) (reaction schemes (Figure 7)). Test strips are the most simple, portable, and quick way to determine the free chlorine in water. Oxidation reaction of syringaldazine (3,5-dimethyl-4-hydroxybenzalazine) and N,N-diethyl-p-phenylenediamine (DPD) with free chlorine will change the test strips from colorless to purple color [70].

3.1. Spectrophotometry Method. The spectrophotometry method is a quantitative analysis of the transmission or reflection properties of a compound as a function of its wavelength. The intensity of light that passes through a colored sample could measure the percentage of sample transmission, spectral bandwidth, logarithm of sample absorption, and percentage of reflectance measurement. Spectrophotometry uses a spectrophotometer which interacts with visible light, near ultraviolet, and/or near infrared. The absorption of light is due to the interaction between the vibrational modes and electronics of the molecules. There are two types of spectrophotometers which are commonly used, namely, single- and double-beam spectrophotometers [71]. The double-beam spectrophotometer has two passages for light to pass through. One passage is for the reference sample, and the other is for the tested sample. Thus, the measurements are made simultaneously. While for the single-beam device, it measures the intensities of light before and after the tested sample is inserted. Thus, measurements are sequential.

The ultraviolet-visible (UV-Vis) spectroscopy method is a quantitative analytical technique used for the determination of an analyte in a liquid or gas phase by absorption of near-ultraviolet (180-390 nm) or visible radiation (390-780 nm) [71]. By using Beer's law, the amount of radiation absorbed is directly related to the concentration of the analyte in solution. This method is considered an economical, fast, and simple on-site Cl_2 monitoring method. The results are less complicated and straightforward without further calculations or analysis needed.

According to Mesquita and Rangel, the detection of chlorine using spectrophotometry is based on the colorimetric

reaction between free chlorine and specific or nonspecific reagents, with an oxidizing capacity. Additionally, through the action of oxidants, this enables electrochemical detection. From literature, it is known that most of the reagents used contain toxic components and are pollutants. Among the most frequent reagents used is toluidine as it is highly sensitive and specific for chlorine ion determination. Nevertheless, it is also known to be a carcinogenic, toxic, and polluting reagent. Thus, Mesquita and Rangel chose o-dianisidine as the reagent to use as it is noncarcinogenic, has low toxicity, and has good sensitivity for chlorine ion determination. However, o-dianisidine is known to have low selectivity. To overcome this, the researchers discovered that to avoid interference, they had to separate the free Cl_2 from the sample. This separation was based on the ability of the free Cl_2 , which is in the form of molecular Cl_2 , a gas at room temperature, to be isolated from the sample through a diffusion membrane. The sample thus must undergo acidification with HCl to ensure that all free chlorine is in molecular chlorine form. Then, the dissolved gas will diffuse from the sample through a hydrophobic membrane in a gas diffusion unit. The diffusion of chlorine gas is then converted to hypochlorite using hydroxide before reacting with o-dianisidine thus resulting in a colored product being measured [69].

A novel approach to selectively detect Cl_2 using a combination of metal nanoparticle paper strips (colorimetric method) and dynamic gas extraction system was developed by Apyari et al. (2018). In this work, there were 3 different silver triangular nanoplate (AgTNP) metal strips each being 0.09, 0.18, and 0.27 mg/g. The strips were prepared using the drop cast method onto paper disks of Whatman Grade 113 and installed into a dynamic gas extraction set for the detection of chlorine gas in a range from 0 to 2.0 mg/L. Based on the results they obtained, increments of the amount of AgTNP on the paper strips increased the sensitivity of chlorine absorption; thus, it was determined that 0.27 mg/g AgTNP paper strip was most suitable for use in selectivity evaluation. The mechanism of dynamic gas extraction was based on the volatility of the compound that passed through the paper strip. The nonvolatile or inert gas is unable to penetrate the paper; therefore, other than the Cl_2 gas, no other significant effect was observed on the paper strip. These results thus promote a useful alternative for a chlorine sensor through the resolution of the selectivity problem [72].

3.2. Solid-State Sensor Methods. Solid-state sensors are based on the principle of a galvanic cell design that contains three components: (1) cathode electrode, (2) anode electrode, and

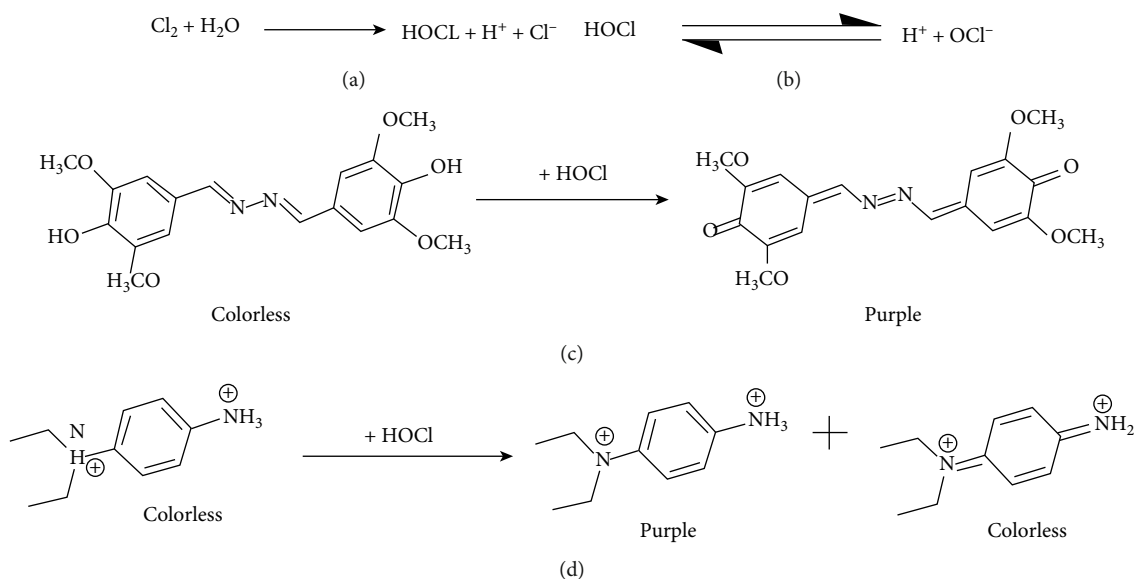


FIGURE 7: (a) Chlorine gas hydrolyses in water to hypochlorous acid. (b) The ratio of hypochlorous acid to hypochlorite ion varies dependent on the pH in aqueous solution. (c) Oxidation reaction of SA with free chlorine and (d) oxidation reaction of DPD with free chlorine [70].

(3) solid electrolyte material. The choice of electrode and electrolyte material is dependent on the application use of the sensor. Normally, during operation, the sensing material is heated to 250°C-350°C, and when the gas analyte is exposed onto the sensing material, the gas resistance will either increase or decrease whereupon this resistance can be measured. The high operating temperature and the modification of sensing materials such as through the addition of dopants and the microstructure/nanostructure of the sensing material used would thus make it selective to the desired gas measurement. This approach has been found to be capable of better sensitivity and recovery of the sensing material towards the gas being measured [73]. However, the calibration needs to maintain consistently in order to avoid fouling of the sensing material or false detection to ensure the long-term usability and stability of the sensor.

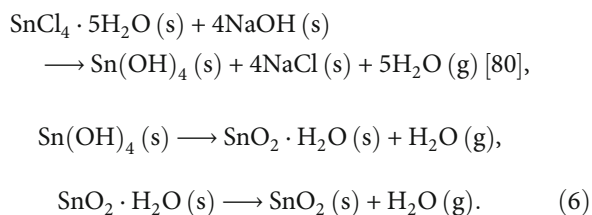
3.2.1. Metal Oxide Sensors. Metal oxide sensors (MOS) rely on the properties of metal oxides at elevated temperatures to change their surface potential, therefore changing their conductivity in the presence of various gases. MOS are the most explored gas sensors due to certain outstanding properties such as high sensitivity, fast response, and good selectivity [74]. The common metal oxides used as sensing materials include zinc oxide (ZnO), tin oxides (SnO₂), iron (Fe₂O₃), zirconium (ZrO₂), titanium (TiO₂), and wolfram (WO₃). These are semiconductor materials and may be either *p*- or *n*-type (with preference to *n*-type). The main advantages of MOS are that the fabrication of the sensor is relatively simple and is highly sensitive due to their operating temperature being between 200 and 500°C. Good metal oxide gas sensors have certain characteristics as follows [41]:

- (1) A high MOS surface area: to maximize the interaction between gas analytes and the sensing surface

- (2) Size and geometry of material: to ensure the movement of electrons and holes in the semiconductor
- (3) High crystallinity and ability for noble metal doping: to improve the performance as a sensing material

As a result, numerous researchers have used metal oxides as the sensitive layer in their sensing materials. Commonly, this type of metal oxide semiconductor sensor is used for detection of chlorine in gaseous form. It is due to the fundamental of the detection based on adsorption. Volatility of the gas analyte is an important factor in determining the response of the sensing material. Fiedot et al. evaluated the influence of microstructures and shape of ZnO as a resistive sensing layer for chlorine detection. Three different synthesized methods were used, which were screen printing, chemical bath deposition (CBD), and electrical CBD (E-CBD). The CBD and E-CBD methods produced quasispherical 1D structures, and crystallization from solution in the presence of an electrical field was easier than recrystallization in paste which leads to smaller particle sizes and a more organized ZnO structure. The detection of Cl₂ gas was conducted using the temperature-stimulated conductance (TSC) method at 250°C to 750°C in the presence of 2 ppm of chlorine. The results revealed that by decreasing the particle size, the sensitivity of the ZnO sensor increased, and it was found that the E-CBD method showed the highest sensitivity and conductivity [75]. Ma et al. used indium oxide (In₂O₃) microtubules which were prepared in a simple two-step immersion-calcination process. The high surface area, abundant oxygen vacancies, and low band gap give outstanding performance for the In₂O₃ Cl₂ gas sensor. This sensor was operated at a high elevated temperature (200°C) to detect 10 ppm of Cl₂ [76]. The same research group then developed In₂O₃ porous hollow rods (PHR) in a metal organic framework (MOF) as a template using a two-step synthetic strategy

by the hydrothermal method. The In_2O_3 porous hollow rods (PHR) showed tremendous performance by achieving optimum operating temperature at 160°C , which was lower than the other most reported MOS. Furthermore, the sensor achieved excellent sensitivity and good selectivity among other gases (acetone, ammonia, nitrogen dioxide, ethanol, and formaldehyde), with a detection limit as lower as 0.5 ppm and a fast response/recovery time (less than 40 s). The morphology of hexagonal hollow rods with a porous structure contributed to the efficiency of In_2O_3 PHR as a Cl_2 gas sensor [77]. Dang et al. fabricated a nanowire sensor using three types of metal oxides, namely, tin oxide (SnO_2), ZnO, and tungsten oxide (WO_3). The SnO_2 sensor achieved better sensitivity as compared to ZnO and WO_3 . Even though the sensors could detect ppb levels of Cl_2 concentration, the optimum operating temperature was 50°C [78]. Zhang et al. also fabricated a three-dimensional open porous tin oxide- (3D OP- SnO_2 -) based gas sensor by grinding together three materials which were tin tetrachloride pentahydrate, sodium hydroxide (NaOH), and sodium chloride (NaCl). The mechanism of formation of the 3D OP- SnO_2 is illustrated in equation (6). Comparison of its performance as a chlorine sensor was conducted using bulk SnO_2 and 3D OP- SnO_2 -based gas sensors to evaluate the effect size of particles towards 5 ppm of chlorine when sensing at 160°C operating temperature. The OP- SnO_2 sensor showed a higher sensitivity and good selectivity among other oxidative gases, with 86% of sensor response maintained for more than 30 days and a fast response as well as a shorter recovery time. The mechanism of these sensors was based on chemisorption which occurred from the dissociation of Cl_2 and desorption of the semiconducting oxide. There are three factors that contribute to the remarkable performance of the OP- SnO_2 sensor which were grain size, a larger surface area, and presence of oxygen vacancies for gas adsorption thus providing an abundant active site, and lastly the unique open porous three-dimensional nanostructure helped the gas molecules to diffuse effectively [79].



Wang et al. synthesized three different nanostructures of tungsten oxide (WO_3), i.e., as nanoparticles, nanorods, and nanoflakes using the facile solvothermal method by varying their solvents. The operating temperature of the nanoparticles was 140°C , while that of the nanorods and nanoflakes was 100°C . The WO_3 nanoparticles exhibited excellent performance in terms of high sensitivity and fast response and recovery time (less than 50 s) and had good reproducibility and selectivity due to the loose structure of the nanoparticles providing abundant sites for gas diffusion. The WO_3 nanostructured sensor was an *n*-type semiconductor sensor where its mechanism was based on the modulation of the

depletion layer by oxygen adsorption. During the gas sensing process, higher oxygen vacancies in the nanoparticles strengthened the interaction between the sensing surface and gas analyte, thus providing better chlorine sensing performance compared to the other two materials [81]. The mechanism of WO_3 sensing with different oxygen vacancy concentrations is illustrated in Figure 8.

However, some of metal oxide sensors have drawbacks such as their need to be operated at high elevated temperatures which leads to high power consumption and thus high cost. Recently, through some improvisation in the preparation of the MOS, some could be operated at room temperatures which would reduce their operating and maintenance costs. Zhao et al. discovered a Cl_2 gas sensor utilizing cadmium stannate (CdSnO_3) that had a fast response, good sensitivity, and excellent selectivity and could function at room temperature. This gas sensor was fabricated by calcining the $\text{CdSnO}_3 \cdot 3\text{H}_2\text{O}$ precursor, which was synthesized using a hydrothermal method, at 550°C . Chemical coprecipitation is the most common technique for producing CdSnO_3 ; however, other procedures may produce products with varied properties and morphologies that may be useful. The results revealed that the CdSnO_3 gas sensor was able to sense 1-10 ppm of Cl_2 gas at room temperature, with good selectivity and quick response behaviour [82]. Apart from that, Choi et al. synthesized single-walled carbon nanotubes (SWCNT) functionalized with platinum (Pt) nanoparticles as a chlorine gas sensor via photoreduction using the ultraviolet (UV) irradiation method. The exposure time and UV irradiation intensity influenced the formation behaviour of the Pt nanoparticles on SWCNT sidewalls in terms of their density and diameter. The sensing performance of the Pt-SWCNT-based gas sensor was evaluated in a mixture of gases (chlorine, nitrogen dioxide, carbon monoxide, and ammonia). The performance of an ideal gas sensor such as high sensitivity (32% at 0.1 ppm) and good selectivity and reproducibility (stable for a 6-month period), operating at room temperature and low detection limits (65 ppb), was achieved successfully. There are few mechanisms involved in the selective sensing of chlorine gas using Pt-SWCNT. At first, the conduction channels of the SWCNT are expanded due to the dissociation of Cl_2 , and this led to a decrease in resistance (reverse flow of electron). Furthermore, Pt nanoparticles had a lower reaction barrier as compared to other metals, and there was a smaller size of these nanoparticles present. This contributes to the continuous electrical connection between SWCNT. Thus, it enhanced the efficiency of electron transfer and increased sensor response. Catalytic Pt nanoparticles also played a major role in the selective detection of Cl_2 on SWCNT mats [83]. Rao et al. also fabricated a chlorine sensor that operated at room temperature using Pd doped with nickel ferrite films as the sensing material. The presence of nickel ferrite gave magnetic properties to this *p*-type semiconductor MOS. This contributed to fast response, long-term stability, and shorter recovery in its detection of 1 ppm Cl_2 gas [21]. Table 3 summarizes the metal oxide-based chlorine sensor.

Band structures are a representation of the allowed electronic energy levels of solid materials and are used to better

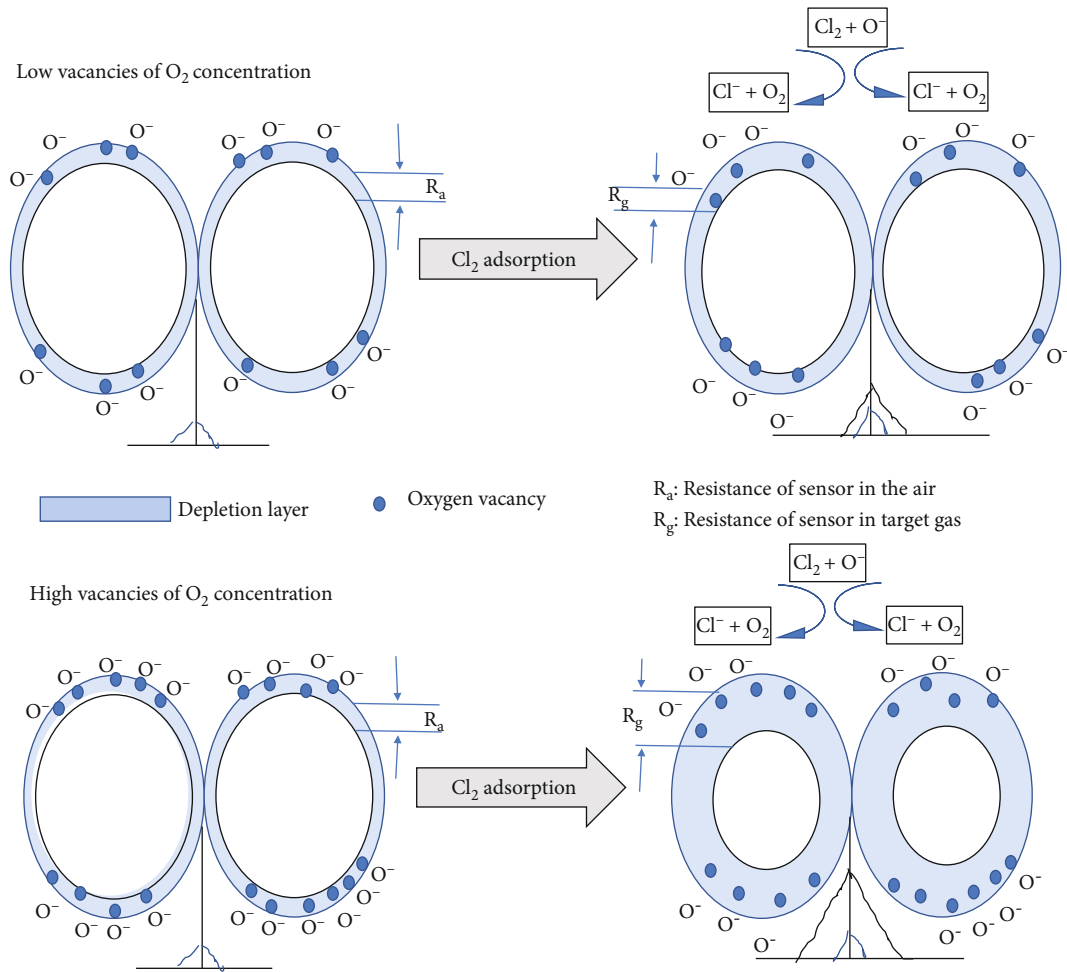


FIGURE 8: Mechanism of WO_3 sensing with different oxygen vacancy concentrations [81].

inform their electrical properties. A band structure is a 2D representation of the energies of the crystal orbitals in a crystalline material. It basically explains the relationship between the energy and momentum of a carrier in a solid. For an electron in free space, the energy is proportional to the square of the momentum. Energy band can be classified into three types: conduction band, valence band, and forbidden energy gap. These energy bands will categorize the electrical properties of solid which are insulator, semiconductor, and conductor. In metal oxide, we need the semiconductor properties to ensure the effectiveness of chlorine gas detection. Semiconductor interfaces can be organized into three types of heterojunctions: straddling gap (type I), staggered gap (type II), or broken gap (type III) [84]. The energy of the carriers at least one of the band edges must change as those carriers pass through the heterojunction. Most often, there will be discontinuities in both the conduction and valence band as shown in Figure 9(a). These discontinuities are the origin of most of the useful properties of heterojunctions. In the semiconductor, there are two types of junctions which are n -type and p -type junctions, depending on the energy in the Fermi level. For the n -type semiconductor, major carriers are electrons, while in p -type semiconductors, hole is

the major carriers [2]. If the semiconductor Fermi level is higher than the redox Fermi level, as is usually the case for n -type semiconductors, then electrons will flow from the semiconductor to the electrolyte and thus the semiconductor Fermi level moves down until it aligns with the redox Fermi level as shown in Figure 9(b). This transfer of electrons bends the bands upwards and creates a layer near the semiconductor surface that is depleted of electrons, the aptly named depletion layer. The scenario is vice versa for p -type semiconductors, where holes flow from the semiconductor to the electrolyte, thereby raising the semiconductor Fermi level until it equals the redox Fermi level (Figure 9(c)) [85].

3.2.2. Conducting Polymers. Basically, polymers are insulators in their neutral state. The insulating properties of polymers have been used extensively in electronic applications. Most conducting polymers are obtained from the reduction or oxidation of neutral polymers. Figure 10 demonstrates examples of typical conducting polymers which act as an active sensing material in gas sensors. These conducting materials have shown a considerable performance such as their strong sensitivity to a wide range of analytes at ambient temperatures, and because the structure of the polymer can

TABLE 3

Material	Findings	Ref.
Zinc oxide synthesized using three different methods: screen printing, chemical bath deposition, and electrical chemical bath deposition (E-CBD)	(i) Smaller particle size leads to increasing the sensitivity and conductivity of the material (ii) E-CBD method produces smaller ZnO particles resulting in being the best method for synthesizing ZnO	[75]
Indium oxide microtubules prepared by the immersion-calcination process using degreasing cotton as soft biotemplates	(i) The sensor displayed high sensitivity and selectivity due to the high surface area, abundant oxygen vacancies, and low band gap (ii) Hollow morphology leads to outstanding performance	[76]
Indium oxide produced using the hydrothermal method	(i) The sensor operated at lower operating temperature (160°C) at most MOS sensor (ii) Excellent sensitivity and good selectivity among other gases (acetone, ammonia, nitrogen dioxide, ethanol, and formaldehyde) (iii) Detection limit as lower as 0.5 ppm and a fast response/recovery time (less than 40 s)	[77]
Tin oxide, zinc oxide, and tungsten oxide prepared by the on-chip growth technique with chemical vapour deposition	(i) SnO ₂ exhibited better performance than WO ₂ and ZnO (5 ppb of chlorine gas at 50°C) (ii) The chlorine gas was adsorbed on the metal oxide surface and then substituted with preadsorbed oxygen, followed by lattice oxygen	[78]
Three-dimensional tin oxide	(i) Small grain size, high surface area, and presence of oxygen vacancies lead to high gas adsorption (ii) Unique open porous three-dimensional nanostructure helped the gas molecules to diffuse effectively	[79]
Three different nanostructures of tungsten oxide (WO ₃), i.e., as nanoparticles, nanorods, and nanoflakes	(i) WO ₃ nanoparticles exhibited better performance than others due to loosen structure of the nanoparticles providing abundant sites for gas diffusion	[81]
Cadmium stannate (CdSnO ₃) produced by the hydrothermal method	(i) Able to detect 1-10 ppm chlorine gas at room temperature (ii) Displays good selectivity and quick response behaviour	[82]
Single-walled CNT functionalized with platinum, Pt nanoparticles	(i) Good selectivity among other gases (ammonia, nitrogen dioxide, and carbon monoxide)	[83]
Palladium doped with nickel ferrite films	(i) Magnetic properties of nickel ferrite attributed to the fast response, long-term stability, and shorter recovery of sensing material	[21]

be modified to respond to specific analytes, with their response being based on inherent properties such as electrical conductivity and rate of electron transfer, they require only simple fabrication which then leads to the ability to miniaturize these sensors [3], [86–90]. From these characteristics, Sivakamasundari et al. developed chlorine sensors using poly(norborene)s bound to cyanuric acid as a polymer film and attached it onto a glass substrate for use as a sensor membrane. The film was then used to measure absorbance intensity during interaction between cyanuric acid and free chlorine [91]. Semenistaya et al. implemented silver (Ag) nanoparticles in polyacrylonitrile (PAN) using infrared (IR) pyrolysis to detect chlorine at room temperature. PAN was chosen based on several advantages including solubility in polar solvents, ability to form a thin film sensor, and change of electrophysical properties from being dielectric to semimetal under IR annealing. Response, sensitivity based on choice of the deposition method, stability, recovery, and effect on air humidity were studied to examine the performance of the Ag-PAN-based chlorine sensor. The sensor showed an increase in conductivity upon exposure of Cl₂ gas, as Cl₂ is a gas oxidizer and acceptor of electron, decreas-

ing the hole concentration in sensing material. The reaction mechanism of chlorine detection pointing to the sensing material is a *p*-type semiconductor characteristic [92].

Sultan et al. fabricated a toxic chlorine sensor using polypyrrole (PPy) as the sensing film. The polymer was functionalized with silicon carbide nanocomposites (SiC) and dodecylbenzene sulphonic acid (DBSA) via *in situ* polymerization in order to enhance its sensing properties. The PPy-based sensor was found to have the highest sensitivity compared to PPy/SiC and PPy/DBS. However, these materials had poor reproducibility performance. All the sensing measurements were performed at room temperature, and the high mobility of charge carriers from all the polymer composites contributed to the good performance of the sensor [93]. Conducting polymer also could be applied in the determination of free chlorine. For instance, paper-based chemiresistive free chlorine sensors were developed by Qin et al. using poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). The main advantage of this free chlorine sensor was that the fabrication could be conducted at room temperature by untrained personnel and without any special equipment or machines needed. It was found

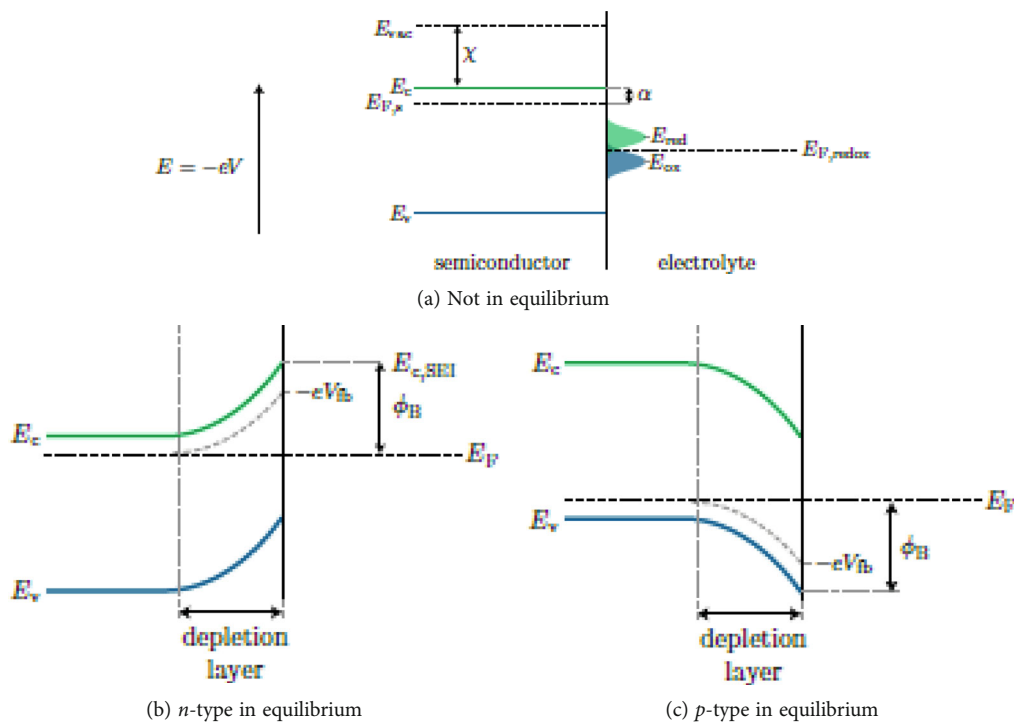


FIGURE 9: Semiconductor interfaces into three different types of heterojunctions [85].

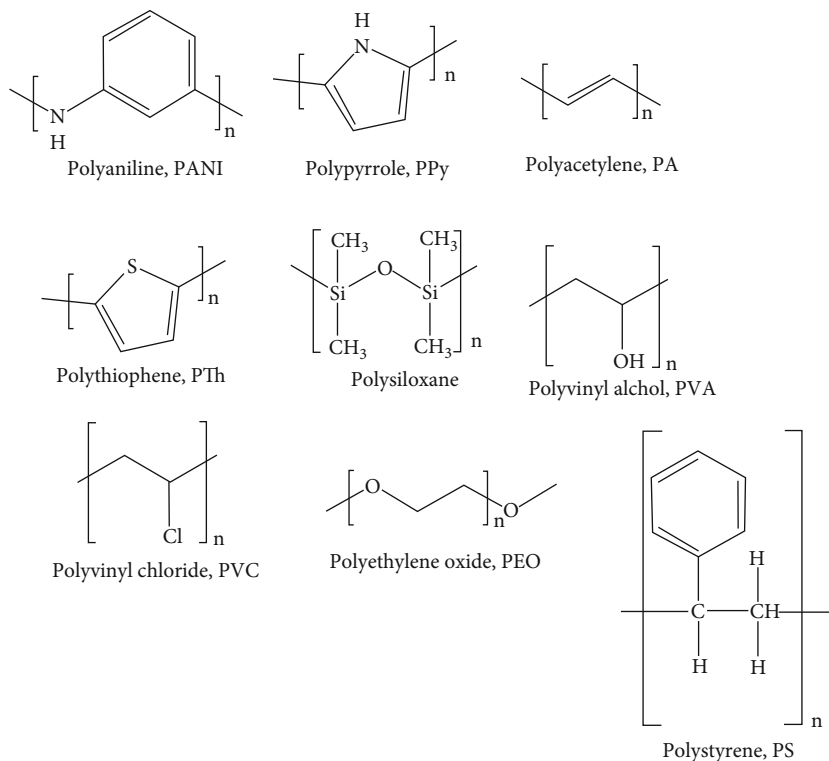


FIGURE 10: Typical conducting polymers used as sensing materials.

to be mechanically stable, had low cost, and was portable which was an advantage for places that had limited fabrication facilities, analytical equipment, and personnel. The performance of the sensor was found to be remarkable with

a wide detection limit range and was reusable [94]. Separately electrochemically reduced graphene oxide (ERGO) was fabricated onto glassy carbon for the electrocatalytic detection of free chlorine by Kumar et al. The ERGO was

electropolymerized using dopamine for 30 cycles to produce a polydopamine-modified electrode (PDA/ERGO). The presence of the quinone functional group on the electrode surface promoted great electrocatalytic ability in the determination of free chlorine [95].

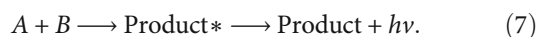
3.3. Optical Methods. Optical methods can also be used to detect free chlorine and chlorine gas due to its high sensitivity and quick response. Basically, optical methods have been identified as being able to differentiate components whose chemical composition and crystalline structure exhibit peculiar behaviour when interacting with the full light spectrum. This behaviour is based on the laws of optics. These interactions are visible to the naked eye when the light radiation involved fall within the visible light spectrum. Optical methods include molecular absorbing spectral analysis, atom spectroscopy, refractometric analysis, and fluorometric analysis. However, optical methods typically need bulky and sophisticated instruments that require a specific place in laboratories [96].

3.3.1. Fibre Optics. An optical-based gas sensor is a device that converts a light ray into an electronic signal. In its simplest form, light which is generated from a light source is passed through an optical fibre and flows to the substrate which is coated with a sensitive layer. The light passing through this substrate is measured for its absorbance, transmittance, or reflectance via an adjacent optical fibre. The advantages of optical-based gas sensors are their immunity from electromagnetic interference, isolation from electrical parameter variations, high durability, real-time monitoring capability, multiple points of care detection feasibilities, and remote analysis practicalities [97]. However, the drawbacks of this sensor is that there are limited choices for the sensitive layer, possible interference from multiple light effects, high cost, and unfamiliarity to end users [98]. Figure 11 shows the basic components of a fibre optic sensor system.

Highly sensitive free chlorine sensors at room temperature were fabricated by Tabassum and Gupta using an optical fibre surface plasma resonance (OFSPR) system. The OFSPR system used interferometers, waveguide methods, and grating couplers as strategies to achieve sensitive chlorine detection capability. Furthermore, this approach was found to have several useful qualities, which included high dependability, ease of use, safety, and a lack of the requirement for an electrical signal to function. The OFSPR was developed using fibre optics coated with polyvinylpyrrolidone (PVP) supported with ZnO deposited over the silver-coated unclad core of the fibre. The combination of ZnO and PVP was due to the presence of plentiful oxygen vacancies and large number of defects in the ZnO, while the PVP had a dielectric function which enhanced the performance of the chlorine sensor. A simple setup was employed to study the behaviour of the Ag/ZnO/PVP-based chlorine sensor. The sensor displayed high sensitivity at 5 nm thickness of the PVP film with a concentration of 5 ppm chlorine [100]. Another free chlorine sensor was developed by Xiong et al. They fabricated a miniaturized microfluidic evanescent-

wave sensor for the colorimetric determination of free Cl₂ in water by integrating a wave sensor on an optical fibre surface and measuring the interaction between the wave and N,N-diethyl-p-phenylenediamine (DPD) reagent. The interaction produced a change of absorbance which can be calculated using Beer's law. The sensor displayed significant capabilities for chlorine determination which were small detection volume (1.2 μL), low detection limit (1.5 ppb), fast response (4.42 s), and excellent repeatability (1.59%) [101]. Later, this work was modified by Usha et al. to develop a more robust chlorine sensor in gaseous form using an optical sensor system. Response improvement was conducted by coating Ag and ZnO in an unclad core of the fibre. Interaction between the metal oxide (at the optimum thickness, Ag (40 nm) and ZnO (18 nm)) and chlorine gas improved the sensitivity of the sensor in concentrations of 10-100 ppm of chlorine gas. Furthermore, the sensor demonstrated a large shift in resonance wavelength (39 nm) during its detection in a mixture of gases indicating that there was higher selectivity towards chlorine gas [102].

3.3.2. Chemiluminescence. Basically, chemiluminescence (CL) is the generation of luminance from the emission of light from an electronically excited state of an element as it returns to its ground state as a result of an oxidation-reduction chemical reaction as illustrated in equation (7) [103]. The CL sensing technique is commonly used in the determination of free chlorine in water due to its simple reaction mechanism. The basic principle of chemiluminescence is depicted in Figure 12.



In CL analysis, micellar and bilayer media have made many important contributions to the improvement of analytical performance and the development of new CL reaction systems. The advantages of CL are that it consists of simple instrumentation, a high sensitivity, wide linear range, and no interference from background scattering light and is versatile for the determination of a wide variety of species. Moreover, CL has become of extensive interest among researchers and has been developed to be a powerful tool in many analytical fields over the past several decades [68]. There are a few hundred organic and inorganic compounds that can be the source of the CL reaction which can arise in the solid phase, liquid phase, liquid-solid phase, gas-solid phase, or gas-liquid phase [10, 15, 104].

Conventionally, in the CL systems, there are chemicals such as luminol, lucigenin, tris(2,2-bipyridine)ruthenium(II), and peroxyoxalate which have been used to determine the concentration of hypochlorite in tap water [105]. Marino and Ingle stated that the luminol reagent generates better sensitivity as compared to other reagents [106]. Ishimaru et al. discovered the effect of luminol-free chlorine CL in an oil-water (*o/w*) microemulsion medium in comparison to that of other reaction media for the determination of free chlorine. This determination was based on the formation of alkyl hypochlorite through the reaction of HOCl with alkyl alcohol (cosurfactant) at the oil-water interface and moves

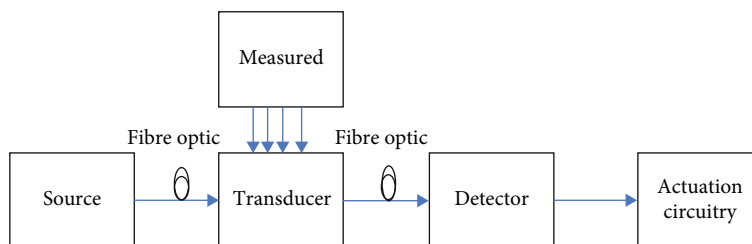


FIGURE 11: Fibre optic sensor system basic components [99].

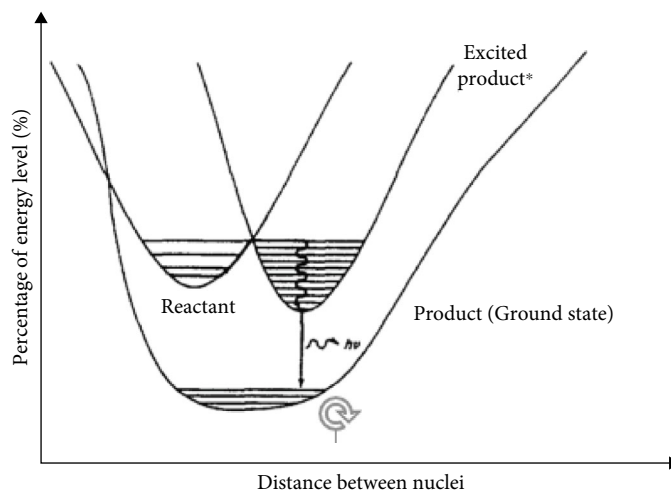


FIGURE 12: Basic principles of the chemiluminescence mechanism.

into the oil phase to oxidize the substrate. However, this kind of reagent is limited in its application due to the use of expensive or poisonous chemicals and has poor selectivity [107].

Nowadays, with promising optical, catalytic, and biocompatible properties, nanomaterials have attracted much attention and they offer new opportunities to CL systems. Tang et al. reported that nanoscale carbon nitrides, such as fluorescent graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) nanosheets and graphitic carbon nitride quantum dots ($g\text{-CNQDs}$), have been explored as fluorescent probes for biological and environment detection due to their distinct optical features. A facile one-step microwave-assisted approach for the preparation of strong fluorescent $g\text{-CNQDs}$ has been developed using guanidine hydrochloride and ethylenediaminetetraacetic acid (EDTA) as the precursors. Interestingly, it was found that a strong CL emission was observed when sodium hypochlorite was injected into the prepared $g\text{-CNQDs}$ [108].

3.4. Electrochemical Sensors. Electrochemical sensors convert a chemical quantity directly into an electrical reading where the chemical reaction or the presence of a chemical product can be measured as an electrical output. The measurement of the electrical output can be varied depending on the substance or reaction which then exhibits a change in resistance (conductivity) or change in capacitance (permittivity). There are few types of electrochemical sensors such as the amperometric sensor (current measurement), potentiometric sensor

(measurement of capacitance and voltage), and conductometric sensor (measurement of conductivity). Normally, electrochemical sensors consist of two electrodes, namely, working and reference electrodes, which interact with an electrolyte, and a thin layer of that electrolyte is sandwiched between the electrodes. The targeted gas will approach and make contact with the electrode where it is either oxidized or reduced at the electrode, thus resulting in a variation of the electrical signal between the electrodes [109].

When used to detect gases, the gas will enter through a thin capillary-type opening and then diffuses over a hydrophobic barrier before finally reaching the electrode surface. The main function of this membrane is to prevent the liquid electrolyte from leaking. Additionally, it also consists of a reference electrode for maintaining a constant and stable potential at the sensing electrode because of the electrochemical reactions occurring incessantly on the electrode surface. The electrochemical reaction with the target gas produces a flow of current flow between the counter and sensing electrodes. The electrolyte is responsible for carrying the ionic charges across the electrode [110]. These electrical signals are dependent on analyte concentration, either linearly or with a logarithmic relationship. Electrochemical sensors are typically larger in size and often more expensive, but the advantages of the electrochemical sensors as compared to metal oxide sensors are their low power consumption, lower detection limits, and good selectivity thus making them more favourable as gas sensors [111].

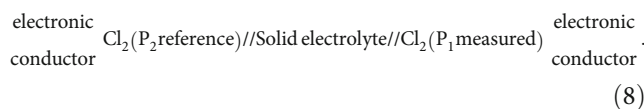
The earliest electrochemical cells were reported by Kohlrausch in 1885 and Haber in the early 1900s [112]. Beginning from that, many researchers started to fabricate electrochemical sensors to detect chlorine gas. In 1999, Pelloux and Godran fabricated a solid-state electrochemical sensor for the detection of chlorine and hydrogen chloride gas. The solid electrolyte used was a chloride ion conductor: PbCl_2 doped with KCl or a two layer SrCl-KClrPbCl-KCl material [113]. Additionally, Sathiyamoorthi et al. evaluated a solid polymer electrolyte which was a plasticized polyethylene oxide- (PEO-) based electrolyte contained within an electrochemical sensor for detecting fluoride and chlorine gas [114]. Previously, several investigations have been reported as regards solid-state electrochemical sensors for Cl_2 gas detection via a metal chloride and $\text{Ag}^+(\beta\beta'')$ alumina as tabulated in Table 4.

3.4.1. Potentiometric Sensor. The group of potentiometric gas sensors has been fabricated with solid electrolyte elements and is thought to be of great benefit as a gas sensor due to their high sensitivity and selectivity, rapid response, and long-term output stability from an electromotive force (emf), which is an open circuit voltage. This emf is produced by the exchange processes of the elemental charge taking place at the interfaces between an electronic and an ionic conductor [120].

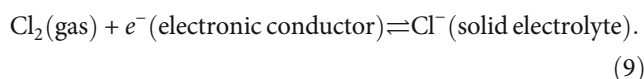
According to Weppner, potentiometric gas sensors can be divided in three general types: type I, type II, and type III.

The type I sensor can be defined as the cell that contains a conducting electrolyte with equilibrium ions compatible with the sensitive gas phase. It is fabricated by sandwiching the electrolyte between two electrodes. The electrolyte used in this cell must be a common species with electrode or gas phase (gas electrode). The emf can be measured by the chemical potential difference between the neutral species and the free mobile ions in the electrolyte system. This type of potentiometric sensor has been successfully fabricated using strontium chloride (SrCl_2) in a potentiometric chlorine gauge [115].

This developed gauge can be represented as



The electrochemical reaction at each electrode is



And the emf between the two electrodes obeys Nerts' law (see the equation below):

$$E = \frac{RT}{2F} \log \frac{P_1 \text{Cl}_2}{P_2 \text{Cl}_2}. \quad (10)$$

Nonetheless, this type of sensor is limited in its detection of species that correspond to the free mobile ionic species found in the electrolyte system.

Type II electrochemical sensors can be defined as a cell that contains electrolytes that have conductivity that is dependent on ions other than those which directly equilibrate with the sensitive gas phase. It utilizes an electrode that provides more flexibility in its detection of chemical species other than the mobile species in the electrolyte. In this sensing system, the chemical potential of the immobile species in the electrolyte can be determined [121]. The galvanic cell of type II setup is depicted in Figure 13.

However, the drawbacks of the type II sensors are that they are still constrained by the limited number of suitable solid ionic conductors containing an immobile species with a known equilibrium reaction with the species to be detected.

Thus, to overcome this disadvantage, the type III sensor was fabricated. It consists of an electrode with a mobile ionic junction between the electrolyte and auxiliary phase (AP). The electrode used can react reversibly. A schematic diagram is depicted in Figure 14.

Generally, the type III potentiometric gas sensors are electrochemical cells that can be described as follows:



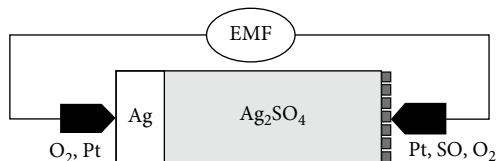
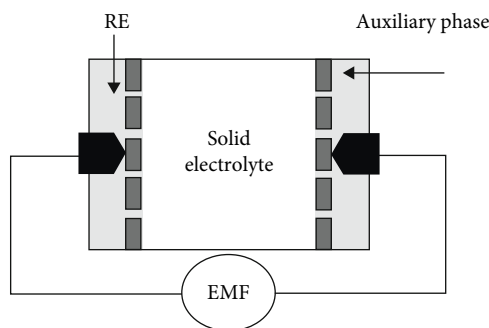
where $X(g)$ denotes the atmosphere containing the detected gas, Me and Me' denote the metallic electrodes, AP denotes the auxiliary phase, SE denotes the solid electrolyte, and B denotes the phase providing the constant potential on the reference electrode.

According to Dziubaniuk et al., performance of type III potentiometric chlorine gas sensor is constructed by polycrystalline sodium superionic conductor (NASICON) with $0.85\text{Na}_2\text{Ti}_3\text{O}_7-0.15\text{Na}_2\text{Ti}_6\text{O}_{13}$ as the reference electrode material and $(1-y)\text{LaOCl}-y\text{NaCl}$ as the AP. The LaOCl electrolyte in this case was doped with Na^+ ions in order to facilitate the occurrence of an electrochemical chain between the SE and AP. The constructed sensor showed its most effective performance at 500°C and with Cl_2 being in a pressure range of 3–9 Pa. Other NASICON electrodes that have been used for potentiometric analysis of chlorine detection were assembled by Han et al. They incorporated chromium oxide (Cr_2O_3) electrodes in a concentration of chlorine gas of 5–50 ppm. The sensor Cr_2O_3 electrodes were sintered at 600°C and showed high sensitivity towards chlorine gas at a temperature of 300°C . Even burying the reference electrode in the middle of the NASICON layer, while decreasing the area of the reference electrode, resulted in the sensitivity improving tremendously thus providing potential alternatives for the application of NASICON with oxide electrodes [123]. Figure 15 depicts the continuous response and recovery as well as repeatability of the NASICON- Cr_2O_3 -based Cl_2 sensor.

Aono and Sadaoka investigated the influence of moisture on potentiometric Cl_2 sensors using a Na^+ conductor with a composite NASICON electrode. The electron number of the

TABLE 4: Solid-state electrochemical sensor using metal chloride and $\text{Ag}^+(\beta' \beta'')$ alumina.

Year	Chlorine gas sensor	Range of concentration detection	Ref.
1985	Potentiometric chlorine gauge	1×10^6 –1 ppm	[115]
1998	Chlorine gas sensors using lead (II) chloride solid electrolyte	10–10 ⁶ ppm	[116]
1992	Cl ₂ gas sensor fabricated from BaCl-KCl solid electrolyte	5 ppm	[117]
1992	Pt Ag Ag ⁺ -β''-alumina AgCl Cl ₂ chlorine gas sensor	100 ppm	[118]
2003	Chlorine gas sensor based on chlorine anion- and scandium (III) cation-conducting solid electrolytes	1%	[119]

FIGURE 13: Schematic diagram of a type II potentiometric sensor (–) Ag, O₂, |Ag₂SO₄|Pt, SO₃, and O₂ (+) [122].FIGURE 14: The schematic structure of type III arrangement. (–) Na₂ZrO₃ + ZrO₂, Au | Na + |Au, and NaNO₃ (+) [122].

electrode reaction ($n = 1.5$) did not agree with the theoretical value ($n = 2.0$). An assumption was made that this may have been due to the Cl[–] ions reacting with moisture at the operating temperature of the sensor. Due to this reason, they examined the sensor under dry and humid conditions. The experimental data obtained from the dry condition test showed an electron number value of 1.86, which was comparable with the theoretical value thus showing that the operating environment of the sensor needs to be controlled. It is postulated that this type of Cl₂ sensor would be useful to detect ppb levels of Cl₂ gas under the environmental conditions found with exhaust gas from an incinerator [124].

3.4.2. Amperometric Sensor. Another type of electrochemical sensor is the amperometric sensor. The amperometric sensor was fabricated based on the “Clark Oxygen Electrode” design which was developed for medical research. Due to the potentiometric sensor expressing a logarithmic property related to the concentration of the gas, its sensitivity, especially at high concentrations, is somewhat low. Amperometric sensors produce a linear output, which would be more suitable for the sensing of high gas concentrations [122].

The amperometric sensor is an electrochemical device in which the current flowing through the system is related to the concentration of the gaseous species [120]. Basically, amperometry consists of a two-electrode configuration (Figure 16). However, since there are limits to the concentrations of the reactant gas, a three-electrode scheme was developed (Figure 17). In the three-electrode configuration, the current at the sensing electrode can be measured with a constant potential condition which generates a genuine thermodynamic potential for all reactions without the involvement of a reference electrode. This is commonly known as “constant-potential amperometry.” When exposed to a vapour or gas that consists of an electroactive analyte, the amperometric gas sensor generates a current due to the diffusion of the analyte into electrochemical cell. Initially, the analyte will diffuse to the working electrode surface then to the working electrode surface and there on will participate in an electrochemical reaction that either accepts or produces electrons. The current produced as a result of the target gas at the sensing or working electrode is measured as the sensor signal which can then be quantified at either a fixed or variable electrode potential [125]. Selectivity to certain gaseous analytes is an important consideration for sensing applications. Thus, amperometric sensors used for detecting various gases can be managed by changing the type of electrolyte used.

An amperometric sensor is usually used in the determination of chlorine gas when it reacts in water. As previously mentioned, reaction of Cl₂ with water (H₂O) leads to the formation of hypochlorous acid (HOCl) and hydrochloric acid (HCl). As hydrochloric acid is a strong acid, it causes a reduction in the pH value, if there is no buffering action in the water. Due to this motivation, an approach proposed by Tomei et al. utilized an amperometric sensor to detect free chlorine in swimming pool water. Carbon black was drop casted onto electrodes and acted as a working electrode modifier at low applied potentials, to overcome any fouling issues. Two important sensor characteristics were evaluated in this study: the sensitivity of the sensor and its limits of detection. By carefully examining the data, it was found that the ability of the sensor to detect free chlorine was in a linear range of 0.05–200 ppm with a detection limit of 0.01 ppm in standard solution as well as in swimming pool water [126]. Prussian blue screen-printed carbon electrodes (SPCEs/PB-BZT) were used to detect free chlorine in a range 0–3 ppm and were assessed by cyclic voltammetry and constant potential amperometry. The electrodes were incorporated

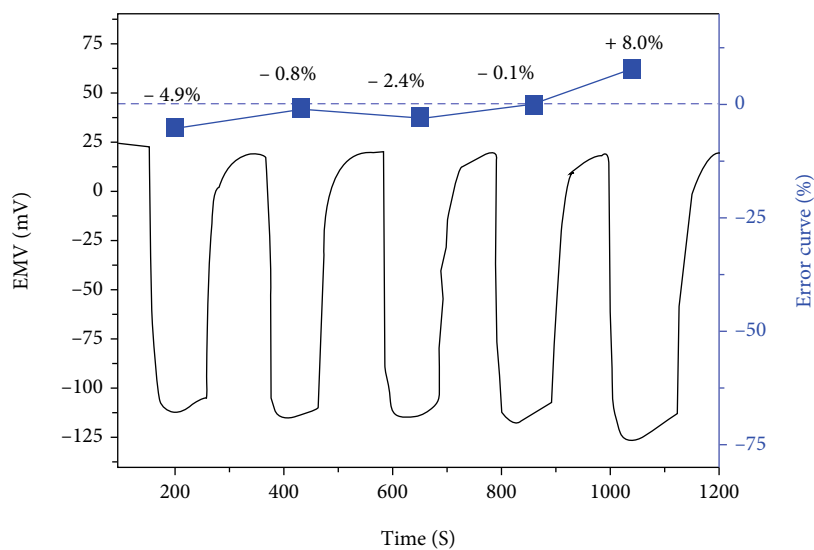


FIGURE 15: Response and recovery of sensor towards 10 ppm Cl_2 gas and repeatability of the Cl_2 sensor [123].

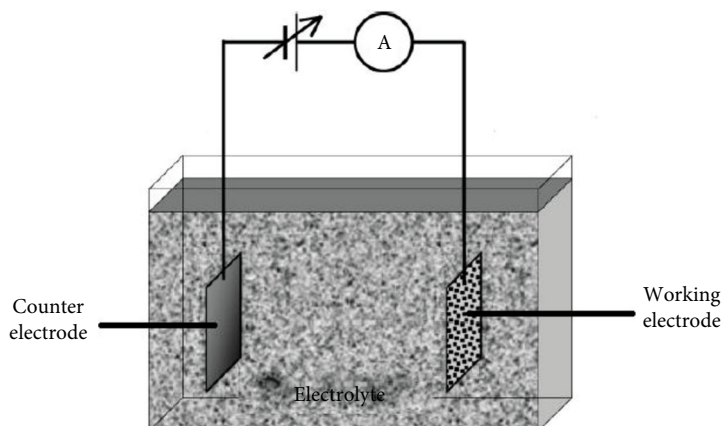


FIGURE 16: Amperometric sensor with a two-electrode configuration [120].

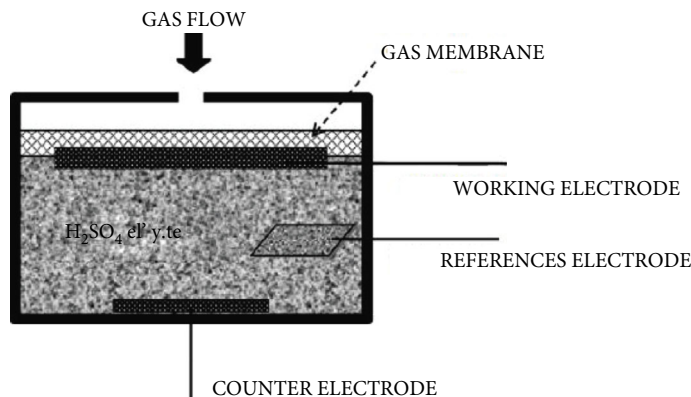


FIGURE 17: Amperometric gas sensor with a three-electrode configuration [120].

in a flow injection device, and this managed to produce high sensitivity ($16.2 \mu\text{A ppm}^{-1} \text{cm}^{-2}$) which made it feasible to be applied for real chlorine analysis samples such as tap water or commercial bleach samples [127]. A fast, sensitive, and reproducible method for chloride ion detection in raw milk

was determined using amperometry analysis through the modification of gold (Au) electrodes and incorporated into a flow injection system. The results demonstrated that the detection limit achieved was 0.005 g/L , detection time 150 ms , oxidation time 550 ms , and reduction time 400 ms .

The modification of the Au electrode proved that this method had potential for the determination of chloride ion concentrations in raw milk samples without preprocessing [128].

3.4.3. Metal Phthalocyanine. Phthalocyanine is an organic substance which is a synthetic analogue of naturally generated porphyrins. There has been substantial interest in the study of thin film forms for use as the active layer in gas sensor devices [129]. Referring to Figure 18, the structure of phthalocyanine is shown as planar aromatic macromolecules that consist of four isoindole units attributed to an 18 π -electron delocalised in an aromatic cloud over alternated nitrogen and carbon sequences. This macrocyclic compound was accidentally synthesized in 1907 as an unidentified blue compound when o-benzamide was heated at a high temperature and was widely used in the dyeing industry as a blue-green-colored dye [130].

The interaction between phthalocyanine and reducing gases as well as oxidizing agents changes their electrical conductivity [132, 133]. Nowadays, since phthalocyanine is insoluble in organic solvents, there are several deposition methods to fabricate unsubstituted phthalocyanine-based gas sensors such as molecular beam epitaxy and glow discharge-induced and sublimation thermal evaporation [134]. Hence, in order to enhance its solubility in wide range of organic solvents, the substitution of the functional group in the phthalocyanine structure has been explored by a number of researchers. Since it can be dissolved in organic solvents, sensors can be fabricated using economical solution processing methods which facilitate self-assembly and spin coating [131].

Previous studies have reported that the phthalocyanine sensor fabricated using a spin coating [135] technique produced a porous morphology that contributed to the faster response of the sensor because of higher rates of adsorption and desorption for the target gases [135–139]. In contrast, various species of central metal ions and their substituent groups can affect the sensitivity of a phthalocyanine sensor [31, 32, 140]. Previously, Co has been used as a central metal, which then demonstrated higher sensitivity (~82% towards 2 ppm with LOD 0.04 ppb) and good selectivity and reproducibility compared to Zn and Cu [141]. The same researcher group has also fabricated metal phthalocyanines using Zn as their central metal modified noncovalently with multiwalled carbon nanotubes (MWCNT). The results revealed that the sensor produced a high sensitivity for Cl₂ detection at ppb level with a response time of less than 20 s [142]. Figure 19 illustrates the response of sensing material in various gases, response of sensing material in different Cl₂ concentrations, sensor response towards Cl₂ gas in different temperatures, and variation in the response of sensor with Cl₂ concentration (experimental curve (dot lines) and fitting curve (solid lines)).

Sharma et al. also fabricated a room temperature Cl₂ sensor using Cu as the central metal. The sensor showed remarkable performance especially with its detection limit as low as 0.27 ppb, a fast response time (9 s towards 2 ppm of Cl₂), and reversibility with baseline recovery. Due to the

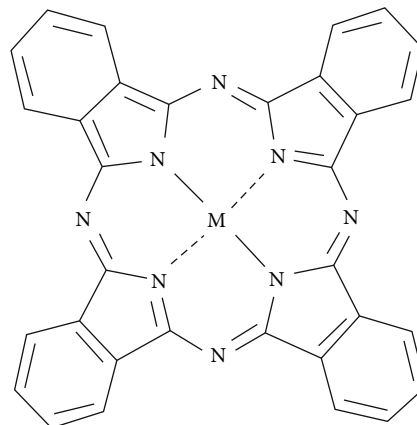
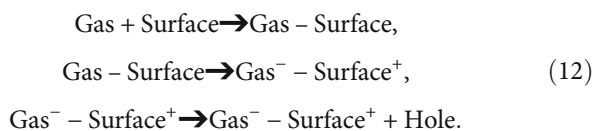


FIGURE 18: Metal phthalocyanine structure [130, 131].

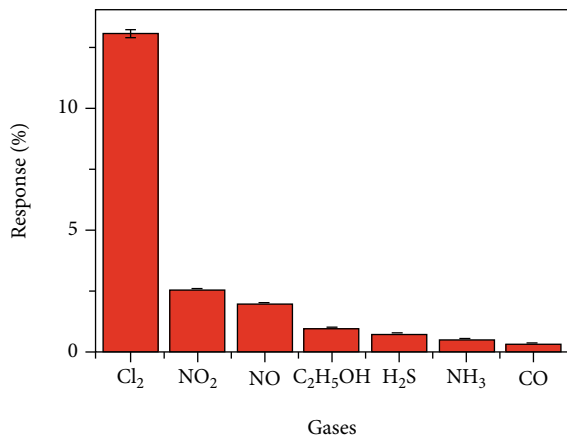
presence of fluorine, the molecular orbital is closer to the Fermi level which promotes an increase in its ionization potential and electron affinity. This would thus lead to better acceptor behaviour which is a significant characteristic for efficient sensor devices [143].

In particular, the electronic properties of metal phthalocyanine (MPc) thin films are known to be affected by the presence of foreign gases. They show high sensitivity towards electrophilic gases that involve chlorine gas. When chlorine gases are adsorbed onto the surface of MPc, the electron withdrawal from the MPc results in the creation of holes and electron delocalisation on the phthalocyanine ring. This phenomenon involves the adsorption of the gas, charge transfer, and hole delocalisation which thus requires activation energy. A simplified description of this phenomena is illustrated in [133, 144]

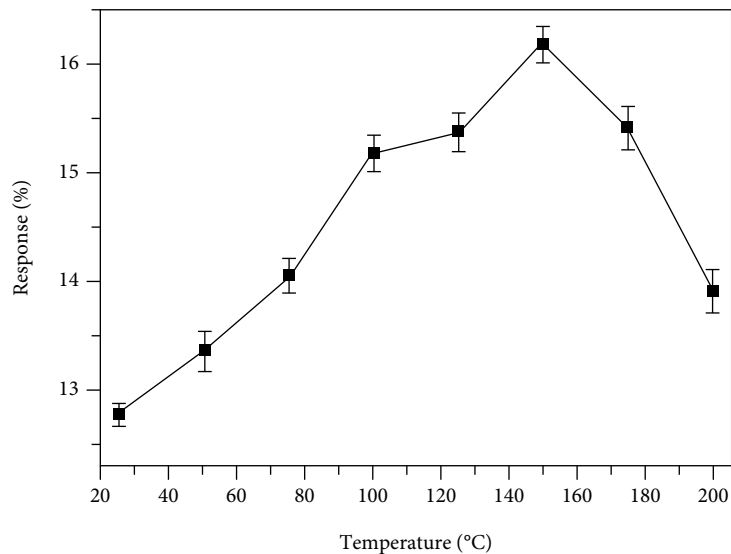


Measurement of conductivity change in the presence of the tested gas is one of the most used parameters in sensor devices using MPc thin films. This type of sensor was developed by Miyata et al. [54]. They revealed the excellent performance of Cu-phthalocyanine (CuPc) thin films which included high sensitivity and a low detection limit (0.18 ppm). Nevertheless, this CuPc thin film gas sensor had several drawbacks such as low sensitivity at operating temperatures above 150°C and the necessity for a heat treatment process for repeated operation. In 2014, these drawbacks were overcome by Saini et al. Saini and coworkers developed Cu-phthalocyanine nanowires to detect Cl₂ gas at the ppb level. The sensor was operated at room temperature and showed an increasing response (91–670%) towards increasing Cl₂ gas concentration (5–1500 ppb) [145].

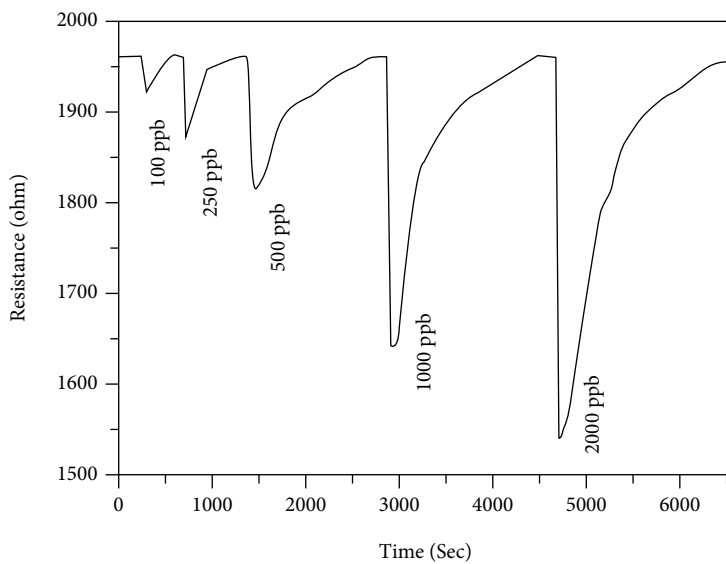
Nonetheless, the temperature of the sensor cannot be increased as the higher temperature would reduce the life span of the sensor. Thus, substituted phthalocyanine was studied in order to fabricate a gas sensor which could work



(a)



(b)



(c)

FIGURE 19: Continued.

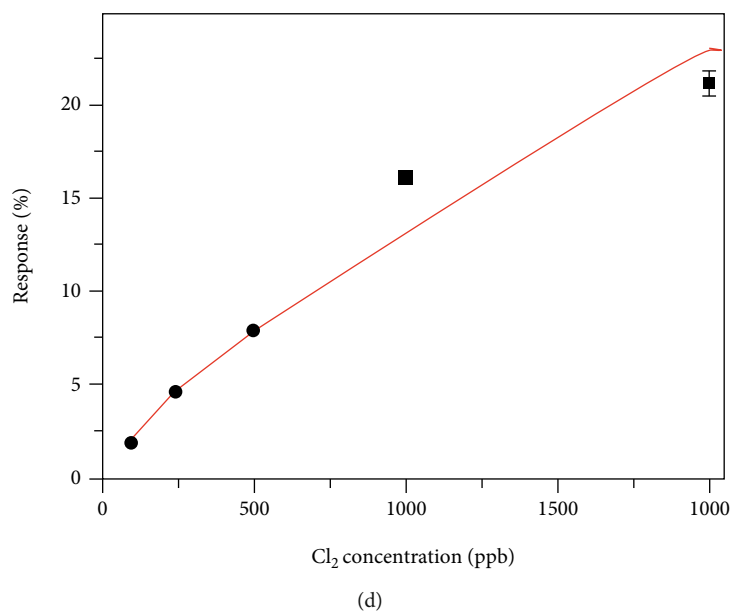


FIGURE 19: (a) Sensor response towards 1 ppm of Cl₂, NO₂, NO, ethanol, hydrogen sulphide, NH₃, and CO. (b) Sensor response towards 1 ppm Cl₂ in different temperatures. (c) Sensor response in different Cl₂ gas concentrations at 150°C. (d) Variation in the response of sensor with Cl₂ concentration (experimental curve (dot lines) and fitting curve (solid lines)).

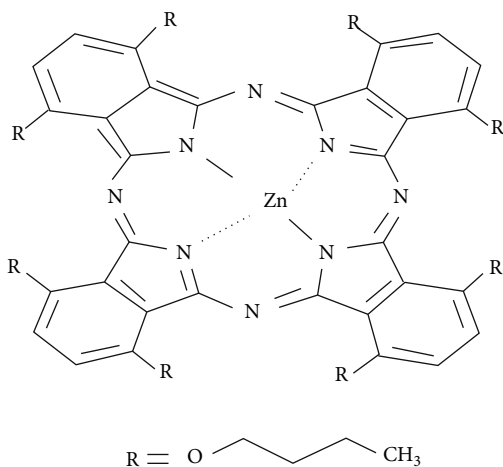


FIGURE 20: Chemical structure of the ZnPc(OBu)₈ molecule [134].

at room temperature and give huge benefit in minimizing the cost of maintenance. Kumar et al. in their study observed the modification of copper phthalocyanine (F₁₆CuPc) with reduced graphene oxide (rGO) as the room temperature Cl₂ sensor. Surface characterization revealed that F₁₆CuPc molecules assembled to form nanoflower-type morphology on rGO sheets. Conductivity of the sensor also improved due to the better charge transfer between Pc ring and rGO sheets where rGO promotes the conducting network. As a result, the sensor produced fast response, good recovery, and high selectivity towards Cl₂ gas. The sensor also works well in room temperature condition [146]. In addition to development, to detect Cl₂ gas at ambient temperature was through a butoxy substitute from a Zn phthalocyanine derivative,

namely, Zn (II) 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine (ZnPc(OBu)₈). The chemical structure is depicted in Figure 20.

Due to its unique chemical structure, it had several advantages:

- (i) An increase in its solubility in various organic solvents due to the presence of butoxy chains, thus reducing the cost of the solution processing method
- (ii) Since the butoxy chain is an electron donor species, it could increase the density of electrons, hence increasing the response towards chlorine gas (oxidizing gas)
- (iii) Butoxy chain substituents can be attributed as spacers among the neighbouring Pc molecules, thus increasing the number of adsorption sites for the chlorine gas which should improve the gas sensing properties of the sensor [134]

3.5. Other Free Chlorine Detection Approaches. According to Watanabe et al., the separation system for the simultaneous direct determination of chlorine dioxide and hypochlorite was established using a laboratory-prepared PTFE tube column packed with Waters Accell QMA as the anion exchange resin. The high-pressure liquid chromatography (HPLC) method described in this work provides a highly effective, quantitative separation of chlorine dioxide and hypochlorite within 3 min. The detection limits of chlorine dioxide and hypochlorite were approximately 0.2 and 10 μg/mL (S/N = 3), respectively. However, this method was found suitable for routine laboratory analysis only [147]. Gas chromatography/mass spectrometry (GC/MS) is

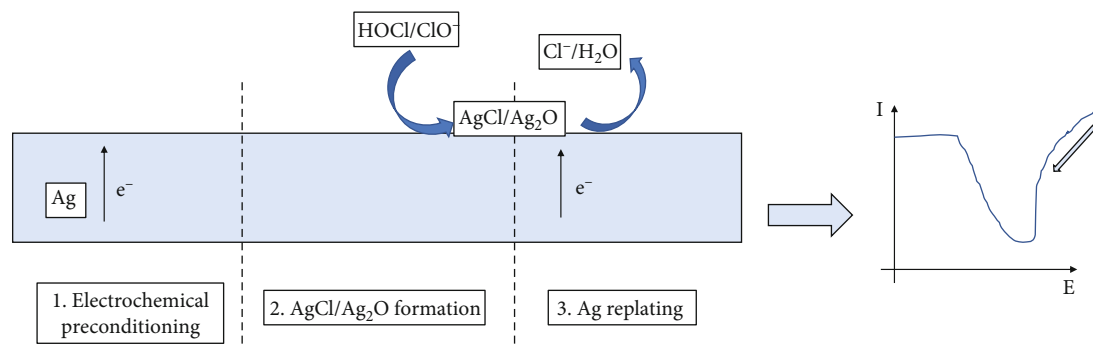


FIGURE 21: Mechanism of detection of free chlorine by inkjet-printed silver electrodes and signal plot obtained from the third step of linear sweep voltammetry [127].

a reliable method because it can identify substances based on both their retention times and mass spectra. Thus, most of guidelines for substance confirmation, such as forensic science and human performance testing confirmation of drugs, workplace testing, and doping in sports, require mass spectrometry-based identification.

Wakigawa et al. reported a rapid and selective GC/MS method to determine free chlorine in an aqueous solution. Using this method, hypochlorous acid was converted into a stable compound because of electrophilic addition. In this work, free chlorine ions were converted into styrene chlorohydrin through electrophilic addition to the styrene in a sodium acetate buffer solution (pH 5). The chlorine derivative obtained was extracted with chloroform and then analyzed by GC/MS [148].

Boron-doped diamond electrode was used to analyze free chlorine concentration developed by Watanabe et al. The reduction of hypochlorite (ClO^-) ions and hypochlorous acid ($HClO$) at the surface of electrode was studied by linear sweep voltammetry (LSV). It was observed that the pH of solution strongly influenced the reduction behaviour due to the different electrochemical activities between ClO^- and $HClO$. $HClO$ reduction proceeds at less negative potential of oxygen reduction reaction via one-electron reduction mechanism. Limit of detection was achieved at $98 \mu g/L$, and the relative standard deviation (RSD) of the peak current for LSV with pretreatment was 45%. Given that there are a few things to improve, these results are encouraging, and the one-electron reduction behaviour is unique to boron-doped diamond electrodes, which have strong selectivity against oxygen reduction reactions and are beneficial for free chlorine identification [149]. Other free chlorine detection using linear sweep voltammetry (LSV) was developed by Milica et al. They fabricated inkjet-printed silver electrodes as working electrodes, $Ag/AgCl$ as reference electrodes, and a platinum wire as the counter electrode. Silver electrodes are often used as reference electrodes because of their small potential window and chemical liability. In this study, the potential of silver acting as the working electrode was investigated due to silver being the cheapest of the noble metals, and its reactivity towards chlorinated species has been promising. As expected, LSV characterization found a linear relationship quantitatively between the amount of

$AgCl/Ag_2O$ produced and concentration of free chlorine in water (1-100 ppm). Figure 21 depicts the mechanism of detection of free chlorine by the inkjet-printed silver electrodes. The study concluded three important findings from their results:

- (1) The sensitivity of the sensor was $30 \mu C/ppm$
- (2) The limit of detection was 2 ppm
- (3) The lowest detectable free chlorine concentration was 0.4 ppm [127]

4. Future Recommendations

Over the past few decades, chlorine sensors have experienced significant development because of the need for effective monitoring of the effects of chlorine on human ecosystems and in water supply systems. However, there are still challenges and limitations that need to be overcome to ensure the efficiency and effectiveness of chlorine determination especially for chlorine gas when reacting in water. One of the drawbacks of current free chlorine sensors is the lack of reversible sensing materials for $HOCl$ and OCl^- . An ideal sensor should either react with free chlorine in a reversible manner or selectively transport $HOCl$ or OCl^- to target substrates. N,N -Diethyl-1,4 phenylenediamine sulphate (DPD) reagents used in optical detection techniques may be the solution to this; however, as yet, this process is still irreversible [150]. The fabrication of chlorine sensors also needs to be rectified in the context of current needs. The synthesis process of CNT, especially single-walled CNT, is expensive and complicated and does negatively affect the environment [151]. Conducting polymers are known for their selectivity performance; however, their solubility and compatibility in solvent media complicate the fabrication of this sensing material. In order to achieve a highly sensitive and fast response sensor, metal oxides need a high operating temperature. Unfortunately, this will shorten their lifespan as a sensor and will require high maintenance costs [152]. Some of the sensing materials used for the determination of chlorine have low discharge energy and poor charge transfer rates and diffusion kinetics. These properties will affect their adsorption capacity during chlorine detection

which would then lead to long response times especially when used in a mixture of multiple gases. Some of the sensors that have been developed also exhibit lower sensitivity which then makes it difficult to detect chlorine in low concentrations.

There are several methods/techniques used to monitor chlorine which depend on an ability to measure output signals. Spectrophotometric methods measure the intensity of light passing through a sample solution, and the concentration of chlorine can be determined from the Beer-Lambert law. Although this method is accurate and simple, the instrument is bulky and not suitable for portable sensing. Solid-state methods including metal oxide and conducting polymer seem to be the most favourable methods to detect chlorine regardless of whether in gaseous or aqueous form. This method measures the output signal in terms of conductivity and resistivity and is dependent on uncontrollable parameters such as humidity and water content in the atmosphere. Electrochemical and optical methods have also shown desirable sensing properties such as their ability to operate at ambient temperature, simple fabrication processes, fast response and recovery times, and high sensitivity. However, the selectivity performance of these sensing materials still needs further exploration in determining if they can be effectively used as real-time monitoring devices.

5. Conclusion

This review discussed the production, application, and dangerous effects of chlorine gas including free chlorine in water towards human beings and the environment. Despite its multiple applications in daily use, this toxic gas does cause serious damage if inhaled and can cause permanent disability and even death. Hence, the detection of chlorine gas is very important both for warning of toxic concentrations in the environment and for monitoring purposes to prevent catastrophes.

Conflicts of Interest

The authors declare that they have no conflict of interest.

Acknowledgments

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References

- [1] M. D. Besmer, J. A. Sigrist, R. Props et al., "Laboratory-scale simulation and real-time tracking of a microbial contamination event and subsequent shock-chlorination in drinking water," *Front. Microbiol.*, vol. 8, no. OCT, pp. 1–11, 2017.
- [2] P. T. Moseley, "Progress in the development of semiconducting metal oxide gas sensors: a review," *Meas. Sci. Technol.*, vol. 28, no. 8, p. 082001, 2017.
- [3] D. Zhang, Z. Wu, and X. Zong, "Flexible and highly sensitive H₂S gas sensor based on in-situ polymerized SnO₂/rGO/PANI ternary nanocomposite with application in halitosis diagnosis," *Sensors and Actuators B: Chemical*, vol. 289, pp. 32–41, 2019.
- [4] G. Singh, A. Choudhary, D. Haranath et al., "ZnO decorated luminescent graphene as a potential gas sensor at room temperature," *Carbon*, vol. 50, no. 2, pp. 385–394, 2012.
- [5] B. Bouchikhi, T. Chludziński, T. Saidi et al., "Formaldehyde detection with chemical gas sensors based on WO₃ nanowires decorated with metal nanoparticles under dark conditions and UV light irradiation," *Sensors Actuators, B Chem.*, vol. 320, p. 128331, 2020.
- [6] R. Kalidoss, S. Umopathy, and Y. Sivalingam, "An investigation of GO-SnO₂-TiO₂ ternary nanocomposite for the detection of acetone in diabetes mellitus patient's breath," *Applied Surface Science*, vol. 449, pp. 677–684, 2018.
- [7] B. Behera and S. Chandra, "Synthesis of nanostructured tungsten oxide by thermal oxidation method and its integration in sensor for VOCs detection," *Advanced Materials Letters*, vol. 7, no. 9, pp. 697–701, 2016.
- [8] C. Tasaltin, M. A. Ebeoglu, and Z. Z. Ozturk, "Acoustoelectric effect on the responses of saw sensors coated with electrospun ZnO nanostructured thin film," *Sensors (Switzerland)*, vol. 12, no. 9, pp. 12006–12015, 2012.
- [9] L. Zhang, Y. Wang, and Q. Q. Ni, "Carbon nanotube template-assisted synthesis of zinc ferrite nanochains," *Materials Chemistry and Physics*, vol. 124, no. 2–3, pp. 1029–1033, 2010.
- [10] N. N. Al-Rawi, B. A. Anwer, N. H. Al-Rawi, A. T. Uthman, and I. S. Ahmed, "Magnetism in drug delivery: the marvels of iron oxides and substituted ferrites nanoparticles," *Saudi Pharm. J.*, vol. 28, no. 7, pp. 876–887, 2020.
- [11] B. Chethan, Y. T. Ravikiran, S. C. Vijayakumari, H. G. Rajprakash, and S. Thomas, "Nickel substituted cadmium ferrite as room temperature operable humidity sensor," *Sensors Actuators, A Phys.*, vol. 280, pp. 466–474, 2018.
- [12] I. C. Sathisha, K. Manjunatha, A. Bajorek et al., "Enhanced humidity sensing and magnetic properties of bismuth doped copper ferrites for humidity sensor applications," *Journal of Alloys and Compounds*, vol. 848, p. 156577, 2020.
- [13] V. Manikandan, M. Singh, B. C. Yadav et al., "Room temperature LPG sensing properties of tin substituted copper ferrite (Sn–CuFe₂O₄) thin film," *Mater. Chem. Phys.*, vol. 240, p. 122265, 2020.
- [14] S. Chakraborty and M. Pal, "Highly efficient novel carbon monoxide gas sensor based on bismuth ferrite nanoparticles for environmental monitoring," *New Journal of Chemistry*, vol. 42, no. 9, pp. 7188–7196, 2018.
- [15] J. Wu, D. Gao, T. Sun et al., "Highly selective gas sensing properties of partially inverted spinel zinc ferrite towards H₂S," *Sensors Actuators, B Chem.*, vol. 235, pp. 258–262, 2016.
- [16] Q. Li, W. Zhang, C. Wang, J. Ma, L. Ning, and H. Fan, "Ag modified bismuth ferrite nanospheres as a chlorine gas sensor," *RSC Advances*, vol. 8, no. 58, pp. 33156–33163, 2018.
- [17] N. Joshi, T. Hayasaka, Y. Liu, H. Liu, O. N. Oliveira, and L. Lin, "A review on chemiresistive room temperature gas sensors based on metal oxide nanostructures, graphene and 2D transition metal dichalcogenides," *Microchim. Acta*, vol. 185, no. 4, p. 213, 2018.

- [18] X. Liu, T. Ma, N. Pinna, and J. Zhang, "Two-dimensional nanostructured materials for gas sensing," *Adv. Funct. Mater.*, vol. 27, no. 37, p. 1702168, 2017.
- [19] Y. Li, Z. Yuan, and F. Meng, "Spinel-type materials used for gas sensing: a review," *Sensors (Basel)*, vol. 20, no. 18, pp. 5413–5422, 2020.
- [20] T. Hashishin, H. Onoda, T. Sanada, D. Fujioka, K. Kojima, and T. Naka, "Magnesium ferrite sensor for H₂S detection," *Sensors and Materials*, vol. 28, no. 11, pp. 1229–1236, 2016.
- [21] P. Rao, R. V. Godbole, and S. Bhagwat, "Chlorine gas sensing performance of palladium doped nickel ferrite thin films," *Journal of Magnetism and Magnetic Materials*, vol. 405, pp. 219–224, 2016.
- [22] P. P. Gauns Dessai, A. K. Singh, and V. M. S. Verenkar, "Mn doped Ni-Zn ferrite thick film as a highly selective and sensitive gas sensor for Cl₂ gas with quick response and recovery time," *Mater. Res. Bull.*, vol. 149, p. 111699, 2022.
- [23] R. R. Powar, V. G. Parale, V. D. Phadtare et al., "Nanocrystalline spinel zinc-substituted cobalt ferrite thick film an efficient ethanol sensor," *Mater. Today Chem.*, vol. 22, p. 100607, 2021.
- [24] S. U. Mutkule, K. K. Tehare, S. K. Gore, K. C. Gunturu, and R. S. Mane, "Ambient temperature operable Bi-Co ferrite NO₂ sensors with high sensitivity and selectivity," *Materials Research Bulletin*, vol. 115, no. 2, pp. 150–158, 2019.
- [25] A. Samal, J. Honovar, C. R. White, and R. P. Patel, "Potential for chlorine gas-induced injury in the extrapulmonary vasculature," *Proceedings of the American Thoracic Society*, vol. 7, no. 4, pp. 290–293, 2010.
- [26] C. W. White and J. G. Martin, "Chlorine gas inhalation human clinical evidence of toxicity and experience in animal models," *Proceedings of the American Thoracic Society*, vol. 7, no. 4, pp. 257–263, 2010.
- [27] P. P. Balte, K. A. Clark, L. C. Mohr, W. J. Karmaus, and E. R. Svendsen, "The immediate clinical picture of acute lung injury following exposure to high concentrations of chlorine gas," *Pulm. Med.*, vol. 2013, pp. A1165–A1165, 2013.
- [28] P. Govier and J. M. Coulson, "Civilian exposure to chlorine gas: a systematic review," *Toxicol. Lett.*, vol. 293, pp. 249–252, 2018.
- [29] M. Dziubaniuk, M. Trzesiec, P. Pasierb, and M. Rekas, "Application of anion-conducting lanthanum oxychloride for potentiometric chlorine gas sensors," *Solid State Ionics*, vol. 225, pp. 324–327, 2012.
- [30] K. E. Fish and J. B. Boxall, "Biofilm microbiome (re)growth dynamics in drinking water distribution systems are impacted by chlorine concentration," *Front. Microbiol.*, vol. 9, pp. 1–21, 2018.
- [31] Z. Witkiewicz, E. Sliwka, and S. Neffé, "Chromatographic analysis of chemical compounds related to the Chemical Weapons Convention," *Trends in Analytical Chemistry*, vol. 85, pp. 21–33, 2016.
- [32] K. Ganesan, S. K. Raza, and R. Vijayaraghavan, "Chemical warfare agents classification of CW agents," *Journal of Pharmacy and BioAllied Sciences*, vol. 2, no. 3, pp. 166–178, 2019.
- [33] S. Polat, M. Gunata, and H. Parlakpinar, "Chemical warfare agents and treatment strategies," *Annals of Medical Research*, vol. 25, no. 4, pp. 776–782, 2018.
- [34] S. Jonasson, B. Koch, and A. Bucht, "Inhalation of chlorine causes long-standing lung inflammation and airway hyperresponsiveness in a murine model of chemical-induced lung injury," *Toxicology*, vol. 303, pp. 34–42, 2013.
- [35] S. M. Brooks and I. L. Bernstein, "Irritant-induced airway disorders," *Immunol. Allergy Clin.*, vol. 31, no. 4, pp. 747–768, 2011.
- [36] R. Megha, F. A. Ali, Y. T. Ravikiran et al., "Conducting polymer nanocomposite based temperature sensors: a review," *Inorg. Chem. Commun.*, vol. 98, pp. 11–28, 2018.
- [37] N. Joshi, L. F. da Silva, H. S. Jadhav et al., "Yolk-shelled ZnCo₂O₄ microspheres: surface properties and gas sensing application," *Sensors Actuators, B Chem.*, vol. 257, pp. 906–915, 2018.
- [38] N. Joshi, L. F. da Silva, H. Jadhav et al., "One-step approach for preparing ozone gas sensors based on hierarchical NiCo₂O₄ structures," *RSC Advances*, vol. 6, no. 95, pp. 92655–92662, 2016.
- [39] N. D. Rudd, H. Wang, E. M. A. Fuentes-Fernandez et al., "Highly efficient luminescent metal-organic framework for the simultaneous detection and removal of heavy metals from water," *ACS Applied Materials & Interfaces*, vol. 8, no. 44, pp. 30294–30303, 2016.
- [40] J. Zhang, X. Liu, G. Neri, and N. Pinna, "Nanostructured materials for room-temperature gas sensors," *Advanced Materials*, vol. 28, no. 5, pp. 795–831, 2016.
- [41] A. Dey, "Semiconductor metal oxide gas sensors: a review," *Mater. Sci. Eng. B*, vol. 229, pp. 206–217, 2018.
- [42] P. R. Lima, A. Mirapalheta, M. Henrique dos Santos Andrade, E. O. Vilar, C. L. P. e Silva Zanta, and J. Tonholo, "Energy loss in electrochemical diaphragm process of chlorine and alkali industry - a collateral effect of the undesirable generation of chlorate," *Energy*, vol. 35, no. 5, pp. 2174–2178, 2010.
- [43] E. M. Almeida Filho, E. O. Vilar, and A. C. O. Feitoza, "Physical-chemical characterization and statistical modeling applied in a chlor-alkali diaphragm-cell process," *Chemical Engineering Research and Design*, vol. 89, no. 4, pp. 491–498, 2011.
- [44] J. H. Shim, J. Y. Jeong, and J. Y. Park, "SWRO brine reuse by diaphragm-type chlor-alkali electrolysis to produce alkali-activated slag," *Desalination*, vol. 413, pp. 10–18, 2017.
- [45] L. C. Brée, K. Perrey, and A. Bulan, "Demand side management and operational mode switching in chlorine production," *Process Syst. Eng.*, vol. 65, no. 7, pp. 1–54, 2019.
- [46] T. Budiarto, E. Esche, J. U. Repke, and E. Leksono, "Dynamic model of chloralkali membrane process," *Procedia Eng.*, vol. 170, pp. 473–481, 2017.
- [47] H. Strathmann, A. Grabowski, and G. Eigenberger, "Ion-exchange membranes in the chemical process industry," *Industrial and Engineering Chemistry Research*, vol. 52, no. 31, pp. 10364–10379, 2013.
- [48] G. P. Thiel, A. Kumar, A. Gómez-González, and J. H. Lienhard, "Utilization of desalination brine for sodium hydroxide production: technologies, engineering principles, recovery limits, and future directions," *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 12, pp. 11147–11162, 2017.
- [49] P. Y. Apel, O. V. Bobreshova, A. V. Volkov et al., *Membranes and Membrane Technologies*, vol. 1, pp. 45–63, 2019.
- [50] A. Eisentraut and A. Brown, "Chlorine," *The Essential Chemical Industry-Online*, 2013.
- [51] F. López-Gálvez, M. I. Gil, P. Truchado, M. V. Selma, and A. Allende, "Cross-contamination of fresh-cut lettuce after a short-term exposure during pre-washing cannot be

- controlled after subsequent washing with chlorine dioxide or sodium hypochlorite,” *Food Microbiology*, vol. 27, no. 2, pp. 199–204, 2010.
- [52] T. Yang, J. Mai, S. Wu et al., “UV/chlorine process for degradation of benzothiazole and benzotriazole in water: efficiency, mechanism and toxicity evaluation,” *Sci. Total Environ.*, vol. 760, p. 144304, 2021.
- [53] K. H. Byun, S. H. Han, J. W. Yoon, S. H. Park, and S. Do Ha, “Efficacy of chlorine-based disinfectants (sodium hypochlorite and chlorine dioxide) on *Salmonella enteritidis* planktonic cells, biofilms on food contact surfaces and chicken skin,” *Food Control*, vol. 123, p. 107838, 2021.
- [54] T. Miyata, S. Kawaguchi, M. Ishii, and T. Minami, “High sensitivity chlorine gas sensors using Cu-phthalocyanine thin films,” *Thin Solid Films*, vol. 425, no. 1-2, pp. 255–259, 2003.
- [55] N. F. Gray, “Chapter thirty-two - chlorine dioxide,” in pp. 591–598, Academic Press, London, 2014, S. L. Percival, M. V Yates, D. W. Williams, R. M. Chalmers, and N. F. B. T.-M. of W. D..
- [56] J. Ding, W. Hua, H. Zhang, and Y. Lou, “The development and application of two chlorine recycling technologies in polyurethane industry,” *Journal of Cleaner Production*, vol. 41, pp. 97–104, 2013.
- [57] A. C. Reddy, “Safety failure criteria of fluorocarbon plastic pipes for dry chlorine transport using finite element analysis,” *Mater. Today Proc.*, vol. 4, no. 8, pp. 7498–7506, 2017.
- [58] X. Yin, M. Yue, Q. Lu et al., “An efficient process for recycling Nd-Fe-B sludge as high-performance sintered magnets,” *Engineering*, vol. 6, no. 2, pp. 165–172, 2020.
- [59] M. Zhang, T. Fujimori, K. Shiota, X. Li, and M. Takaoka, “Formation pathways of polychlorinated dibenzo-p-dioxins and dibenzofurans from burning simulated PVC-coated cable wires,” *Chemosphere*, vol. 264, p. 128542, 2021.
- [60] S. Cheng, S. Wang, and Z. Liu, “Cycle performance of alternative refrigerants for domestic air-conditioning system based on a small finned tube heat exchanger,” *Applied Thermal Engineering*, vol. 64, no. 1–2, pp. 83–92, 2014.
- [61] Y. Li, T. Xia, T. Yu et al., “Nitrogen/chlorine-doped carbon nanodisk-encapsulated hematite nanoparticles for high-performance lithium-ion storage,” *Journal of Alloys and Compounds*, vol. 843, p. 156045, 2020.
- [62] X. Liu, M. Li, X. Yang, X. Zeng, H. Wang, and H. Jiang, “Carbon encapsulation and chlorine doping enable $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ superior sodium ion storage properties as cathode material for sodium ion battery,” *Powder Technology*, vol. 364, pp. 70–77, 2020.
- [63] A. S. Koohestani and A. Bashari, “Advanced bulletproof and stab- and spike-resistant textiles,” LTD, 2020.
- [64] S. Jyothsna, G. Manjula, P. Chandar Rao, D. Sammaiah, and A. S. Nageswara Rao, “Estimation of trace elemental concentration in *Azadirachta indica* and *Withania somnifera* anticancer medicinal plants of Telangana using EDXRF technique,” *Mater. Today Proc.*, vol. 43, pp. 2383–2388, 2020.
- [65] I. Komara, E. Alfa Winata, A. Susanto, and I. Hendiani, “Periodontal tray application of chlorine dioxide gel as an adjunct to scaling and root planing in the treatment of chronic periodontitis,” *Saudi Dent. J.*, vol. 32, no. 4, pp. 194–199, 2020.
- [66] Z. Aminov, R. Haase, R. Rej et al., “Diabetes prevalence in relation to serum concentrations of polychlorinated biphenyl (PCB) congener groups and three chlorinated pesticides in a Native American population,” *Environmental Health Perspectives*, vol. 124, no. 9, pp. 1376–1383, 2016.
- [67] P. Lu, Q. Huang, A. C. T. Bourtsalas, N. J. Themelis, Y. Chi, and J. Yan, “Review on fate of chlorine during thermal processing of solid wastes,” *J. Environ. Sci.*, vol. 78, pp. 13–28, 2019.
- [68] Z.-X. Gao, H. F. Li, J. Liu, and J. M. Lin, “A simple microfluidic chlorine gas sensor based on gas-liquid chemiluminescence of luminol-chlorine system,” *Analytica Chimica Acta*, vol. 622, no. 1-2, pp. 143–149, 2008.
- [69] R. B. R. Mesquita and A. O. S. S. Rangel, “Gas diffusion sequential injection system for the spectrophotometric determination of free chlorine with *o*-dianisidine,” *Talanta*, vol. 68, no. 2, pp. 268–273, 2005.
- [70] K. U. Schwenke, D. Spiehl, M. Krauß et al., “Analysis of free chlorine in aqueous solution at very low concentration with lateral flow tests,” *Scientific Reports*, vol. 9, no. 1, pp. 1–11, 2019.
- [71] P. J. Worsfold and E. A. G. Zagatto, “Spectrophotometry | overview,” in pp. 244–248, Academic Press, Oxford, 2019, P. Worsfold, C. Poole, A. Townshend, and M. B. T.-E. of A. S.
- [72] V. V. Apyari, M. O. Gorbunova, A. V. Shevchenko et al., “Towards highly selective detection using metal nanoparticles: a case of silver triangular nanoplates and chlorine,” *Talanta*, vol. 176, pp. 406–411, 2018.
- [73] G. M. Kale and J. M. Jafferson, “Solid-state gas sensors: design and fabrication,” Elsevier Ltd, 2016, no. November 2015.
- [74] J. Casanova-Cháfer, È. Navarrete, and E. Llobet, “Gas sensing with iridium oxide nanoparticle decorated carbon nanotubes,” *Sensors*, vol. 19, no. 1, p. 113, 2019.
- [75] M. Fiedot, O. Rac, P. S. Wo, and H. Teterycz, “Influence of a morphology sensitive layer of resistive gas sensors on chlorine sensing,” *Procedia Engineering*, vol. 168, pp. 1118–1121, 2016.
- [76] J. Ma, H. Fan, H. Tian et al., “Ultrahigh sensitivity and selectivity chlorine gas sensing of In_2O_3 hollow microtubules by bio-template method with degreasing cotton,” *Sensors Actuators, B Chem.*, vol. 262, pp. 17–25, 2018.
- [77] J. Ma, H. Fan, X. Zheng et al., “Facile metal-organic frameworks-templated fabrication of hollow indium oxide microstructures for chlorine detection at low temperature,” *J. Hazard. Mater.*, vol. 387, no. 127, p. 122017, 2020.
- [78] T. Van Dang, N. Duc Hoa, N. Van Duy, and N. Van Hieu, “Chlorine gas sensing performance of on-chip grown ZnO , WO_3 , and SnO_2 nanowire sensors,” *ACS Applied Materials & Interfaces*, vol. 8, no. 7, pp. 4828–4837, 2016.
- [79] W. Zhang, Q. Li, C. Wang et al., “High sensitivity and selectivity chlorine gas sensors based on 3D open porous SnO_2 synthesized by solid-state method,” *Ceramics International*, vol. 45, no. 16, pp. 20566–20574, 2019.
- [80] A. Gohier, J. Chancelon, P. Chenevier, D. Porterat, M. Mayne-L’Hermite, and C. Reynaud, “Optimized network of multi-walled carbon nanotubes for chemical sensing,” *Nanotechnology*, vol. 22, no. 10, p. 105501, 2011.
- [81] Q. Wang, J. Huang, J. Zhou et al., “Different nanostructured tungsten oxides synthesized by facile solvothermal route for chlorine gas sensing,” *Sensors and Actuators B: Chemical*, vol. 275, pp. 306–311, 2018.
- [82] X. Zhao, Z. Li, X. Lou, M. Li, and N. Zhang, “Room-temperature chlorine gas sensor based on CdSnO_3 synthesized by

- hydrothermal process,” *J. Adv. Ceram.*, vol. 2, no. 1, pp. 31–36, 2013.
- [83] S. W. Choi, B. M. Kim, S. H. Oh, and Y. T. Byun, “Selective detection of chlorine at room temperature utilizing single-walled carbon nanotubes functionalized with platinum nanoparticles synthesized via ultraviolet irradiation,” *Sensors Actuators, B Chem.*, vol. 249, pp. 414–422, 2017.
- [84] N. P. de Moraes, C. M. Goes, D. C. Sperandio et al., “Development of a new zinc oxide/tin oxide/carbon xerogel photocatalyst for visible light photodegradation of 4-chlorophenol,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 269, p. 115183, 2021.
- [85] S. Harrison, *Exploring and Exploiting Charge-Carrier Confinement in Semiconductor Nanostructures: Heterodimensionality in Sub-Monolayer InAs in GaAs Photoelectrolysis Using Type-II Heterojunctions*, [M.S. thesis], Lancaster Univ, 2016.
- [86] C. J. Chiang, K. T. Tsai, Y. H. Lee et al., “In situ fabrication of conducting polymer composite film as a chemical resistive CO₂ gas sensor,” *Microelectronic Engineering*, vol. 111, pp. 409–415, 2013.
- [87] A. Gusain, N. J. Joshi, P. V. Varde, and D. K. Aswal, “Flexible NO gas sensor based on conducting polymer poly[*N*-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT),” *Sensors Actuators, B Chem.*, vol. 239, pp. 734–745, 2017.
- [88] T. Hyodo, C. Ishibashi, K. Matsuo, K. Kaneyasu, H. Yanagi, and Y. Shimizu, “CO and CO₂ sensing properties of electrochemical gas sensors using an anion-conducting polymer as an electrolyte,” *Electrochimica Acta*, vol. 82, pp. 19–25, 2012.
- [89] K. Mahesh, M. Subbaiah, K. S. Nithin, B. M. J. Raj, and S. Shivanna, “Highly flexible and conducting polymer nanocomposite films for selective gas sensing applications,” *Mater. Today Proc.*, vol. 9, pp. 515–521, 2019.
- [90] J. Soloducho and J. Cabaj, “Conducting polymers in sensor design,” *Intech*, vol. i, pp. 28–48, 2012.
- [91] N. Sivakamasundari, N. Bharathi, A. R. Neena Sruthi, and A. B. Ganesh, “Optrode based polymer for the estimation of free chlorine,” *Applied Mechanics and Materials*, vol. 573, pp. 856–860, 2014.
- [92] T. V. Semenistaya, V. V. Petrov, and P. Lu, “Nanocomposite of Ag-polyacrylonitrile as a selective chlorine sensor,” *Advances in Materials Research*, vol. 804, pp. 135–140, 2013.
- [93] A. Sultan, S. Ahmad, and F. Mohammad, “Highly sensitive chlorine gas sensor and enhanced thermal DC electrical conductivity from polypyrrole/silicon carbide nanocomposites,” *RSC Adv.*, vol. 6, no. 87, pp. 84200–84208, 2016.
- [94] Y. Qin, S. Pan, M. M. R. Howlader, R. Ghosh, N. X. Hu, and M. J. Deen, “Paper-based, hand-drawn free chlorine sensor with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate),” *Analytical Chemistry*, vol. 88, no. 21, pp. 10384–10389, 2016.
- [95] D. R. Kumar, S. Kesavan, T. T. Nguyen, J. Hwang, C. Lamiel, and J. Shim, “Polydopamine@electrochemically reduced graphene oxide-modified electrode for electrochemical detection of free-chlorine,” *Sensors and Actuators B: Chemical*, vol. 240, pp. 818–828, 2017.
- [96] F. C. Trigo, O. Sanchez, and F. P. R. Martins, *Application of Optical Techniques to Materials Characterization and Modeling*, S. Hashmi, G. F. Batalha, C. J. Tyne, and B. B. T.-C. M. P. Yilbas, Eds., Elsevier, Oxford, 2014.
- [97] S. P. Usha, A. M. Shrivastav, and B. D. Gupta, “Semiconductor metal oxide/polymer based fiber optic lossy mode resonance sensors: a contemporary study,” *Opt. Fiber Technol.*, vol. 45, pp. 146–166, 2018.
- [98] D. P. Dhiraj Ahuja, “Optical fiber sensors and their applications,” *J. Sci. Res. Rev.*, vol. 1, no. 5, pp. 60–68, 2012.
- [99] N. Sabri, S. A. Aljunid, M. S. Salim, R. B. Ahmad, and R. Kamaruddin, “Toward optical sensors: review and applications,” *J. Phys. Conf. Ser.*, vol. 423, no. 1, p. 012064, 2013.
- [100] R. Tabassum and B. D. Gupta, “Detection of chlorine utilizing polyvinylpyrrolidone supported zinc oxide thin films,” vol. 140, pp. 1863–1870, *Analyst*.
- [101] A. Y. Xiong, J. Tan, C. Wang et al., “A miniaturized evanescent-wave free chlorine sensor based on colorimetric determination by integrating on optical fiber surface,” *Sensors Actuators B. Chem.*, vol. 245, pp. 674–682, 2017.
- [102] S. P. Usha, S. K. Mishra, and B. D. Gupta, “Fabrication and characterization of a SPR based fiber optic sensor for the detection of chlorine gas using silver and zinc oxide,” *Materials*, vol. 8, no. 5, pp. 2204–2216, 2015.
- [103] C. A. Marquette and L. J. Blum, “Applications of the luminol chemiluminescent reaction in analytical chemistry,” *Analytical and Bioanalytical Chemistry*, vol. 385, no. 3, pp. 546–554, 2006.
- [104] U. Isacson and G. Wettermark, “Chemiluminescence in analytical chemistry,” *Analytica Chimica Acta*, vol. 68, no. 2, pp. 339–362, 1974.
- [105] P. S. Francis, N. W. Barnett, S. W. Lewis, and K. F. Lim, “Hypohalites and related oxidants as chemiluminescence reagents: a review,” *Luminescence*, vol. 19, no. 2, pp. 94–115, 2004.
- [106] D. F. Marino and J. D. Ingle, “Determination of chlorine in water by luminol chemiluminescence,” *Analytical Chemistry*, vol. 53, no. 3, pp. 455–458, 1981.
- [107] N. Ishimaru, J. M. Lin, and M. Yamada, “Luminol-free chlorine chemiluminescence in an oil-in-water microemulsion medium,” *Analytical Communications*, vol. 35, no. 2, pp. 67–69, 1998.
- [108] Y. Tang, Y. Su, N. Yang, L. Zhang, and Y. Lv, “Carbon nitride quantum dots: a novel chemiluminescence system for selective detection of free chlorine in water,” *Analytical Chemistry*, vol. 86, no. 9, pp. 4528–4535, 2014.
- [109] C. Dejous, H. Hallil, V. Raimbault, R. Rukkumani, and J. V. Yakhmi, Eds., “Chapter 20 - using microsensors to promote the development of innovative therapeutic nanostructures,” in *Micro and Nano Technologies*, pp. 539–566, Elsevier, 2017, D. Ficaí and A. M. B. T.N. for N. T. Grumezescu.
- [110] Z. Yunusa, “Sensors & transducers gas sensors: a review,” *Sensor and Transducers Journal*, vol. 168, no. 4, pp. 61–75, 2014.
- [111] H. Price, “Air analysis | Field portable instruments for the measurement of airborne hazards,” in pp. 40–43, Academic Press, Oxford, 2019, P. Worsfold, C. Poole, A. Townshend, and M. B. T.-E. of A. S.
- [112] T. Hübert, L. Boon-brett, G. Black, and U. Banach, “Sensors and actuators B: chemical hydrogen sensors – a review,” *Sensors and Actuators B: Chemical*, vol. 157, pp. 329–352, 2011.
- [113] A. Pelloux and C. Gondran, “Solid state electrochemical sensor for chlorine and hydrogen chloride gas trace analysis,” *Sensors and Actuators B: Chemical*, vol. 59, no. 2-3, pp. 83–88, 1999.

- [114] R. Sathiyamoorthi, R. Chandrasekaran, T. Mathanmohan, B. Muralidharan, and T. Vasudevan, "Study of electrochemical based gas sensors for fluorine and chlorine," *Sensors and Actuators B: Chemical*, vol. 99, no. 2-3, pp. 336-339, 2004.
- [115] A. Pelloux, P. Fabry, and P. Durante, "Design and testing of a potentiometric chlorine gauge," *Sensors Actuators, B Chem.*, vol. 7, no. 4, pp. 245-252, 1985.
- [116] Y. Niizeki and S. Shibata, "Room temperature operating solid-state sensor for chlorine gas," *Journal of The Electrochemical Society*, vol. 145, no. 7, pp. 2445-2447, 1998.
- [117] J. Liu and W. Weppner, "Limiting-current type surface modified gas sensor based on β'' -alumina fast solid ionic conductor," *Applied physics. A, Materials science & processing*, vol. 52, no. 2, pp. 94-99, 1991.
- [118] C. M. Mari, G. Terzaghi, M. Bertolini, and G. B. Barbi, "A chlorine gas potentiometric sensor," *Sensors and Actuators B: Chemical*, vol. 8, no. 1, pp. 41-45, 1992.
- [119] N. Imanaka, K. Okamoto, and G. Adachi, "New chlorine gas sensor fabricated from chlorine anion- and scandium(III) cation-conducting solid electrolytes," *Sensors and Actuators B: Chemical*, vol. 93, no. 1-3, pp. 233-236, 2003.
- [120] C. M. Marl and G. B. Barbi, *Electrochemical Gas Sensors* pp. 329-364, Springer.
- [121] C. O. Park, J. W. Fergus, N. Miura, J. Park, and A. Choi, "Solid-state electrochemical gas sensors," *Ionics*, vol. 15, no. 3, pp. 261-284, 2009.
- [122] C. O. Park, M. Science, W. Hall, O. State, and W. Weppner, "Ceramic electrolytes and electrochemical sensors," *Journal of Materials science*, vol. 8, pp. 4639-4660, 2003.
- [123] H. Zhang, J. Li, H. Zhang et al., "NASICON-based potentiometric Cl_2 sensor combining NASICON with Cr_2O_3 sensing electrode," *Sensors Actuators, B Chem.*, vol. 180, no. 3, pp. 66-70, 2013.
- [124] H. Aono and Y. Sadaoka, "Influence of moisture on potentiometric Cl_2 gas sensor using a Na^+ conducting solid electrolyte," *J. Electrochem. Soc.*, vol. 149, no. 6, p. H123, 2002.
- [125] J. R. Stetter, "Amperometric gas sensors: a review," *Chemical reviews*, pp. 352-366, 2008.
- [126] M. R. Tomei, F. Arduini, D. Neagu, and D. Moscone, "Carbon black-based disposable sensor for an on-site detection of free chlorine in swimming pool water," *Talanta*, vol. 189, pp. 262-267, 2018.
- [127] M. Jovi, F. Cortés-salazar, A. Lesch, V. Amstutz, H. Bi, and H. H. Girault, "Electrochemical detection of free chlorine at inkjet printed silver electrodes," *Journal of Electroanalytical Chemistry*, vol. 756, pp. 171-178, 2015.
- [128] X. Chen, B. Chu, H. Xi et al., "Determination of chlorine ions in raw milk by pulsed amperometric detection in a flow injection system," *Journal of Dairy Science*, vol. 101, no. 11, pp. 9647-9658, 2018.
- [129] N. Manjunatha, M. Imadadulla, K. S. Lokesh, and K. R. V. Reddy, "Synthesis and electropolymerization of tetra- $[\beta$ -(2-benzimidazole)] and tetra- $[\beta$ -(2-(1-(4-aminophenyl))benzimidazole)] embedded cobalt phthalocyanine and their supercapacitance behaviour," *Dye. Pigment*, vol. 153, pp. 213-224, 2018.
- [130] J. K. F. Van Staden, "Application of phthalocyanines in flow and sequential-injection analysis and microfluidics systems: a review," *Talanta*, vol. 139, pp. 75-88, 2015.
- [131] G. De Torre and C. G. Claessens, "Phthalocyanines: old dyes, new materials. Putting color in nanotechnology," *ChemInform*, vol. 38, no. 35, 2007.
- [132] N. Kılınc, S. Öztürk, D. Atila, A. G. Gürek, V. Ahsen, and Z. Z. Öztürk, "Electrical and NO_2 sensing properties of liquid crystalline phthalocyanine thin films," *Sensors and Actuators B: Chemical*, vol. 173, no. 2, pp. 203-210, 2012.
- [133] R. Tongpool and S. Yoriya, "Kinetics of nitrogen dioxide exposure in lead phthalocyanine sensors," *Thin Solid Films*, vol. 477, no. 1-2, pp. 148-152, 2005.
- [134] R. Saini, A. Mahajan, R. K. Bedi, D. K. Aswal, and A. K. Debnath, "Solution processed films and nanobelts of substituted zinc phthalocyanine as room temperature ppb level Cl_2 sensors," *Sensors and Actuators B: Chemical*, vol. 198, pp. 164-172, 2014.
- [135] A. K. Ray, "Organic materials for chemical sensing," *Springer Handbook of Electronic and Photonic Materials*, pp. 1281-1310, 2017.
- [136] B. Wang, X. Zuo, Y. Wu, Z. Chen, C. He, and W. Duan, "Comparative gas sensing in copper porphyrin and copper phthalocyanine spin-coating films," *Sensors and Actuators B: Chemical*, vol. 152, no. 2, pp. 191-195, 2011.
- [137] B. Wang, X. Zhou, Y. Wu, Z. Chen, C. He, and X. Zuo, "Preparation, characterization and NH_3 -sensing of 1,8,15,22-tetraiso-pentylxyphthalocyanine copper, nickel and lead spin-coating films," *Sensors and Actuators B: Chemical*, vol. 161, no. 1, pp. 498-503, 2012.
- [138] F. I. Bohrer, C. N. Colesniuc, J. Park et al., "Comparative gas sensing in cobalt, nickel, copper, zinc, and metal-free phthalocyanine chemiresistors," *Journal of the American Chemical Society*, vol. 131, no. 2, pp. 478-485, 2009.
- [139] J. Gao, G. Lu, Y. Chen, and M. Bouvet, "Solution-processed thin films based on sandwich-type mixed (phthalocyaninato)(porphyrinato) europium triple-deckers: structures and comparative performances in ammonia sensing," *Sensors and Actuators B: Chemical*, vol. 166-167, pp. 500-507, 2012.
- [140] Z. Jie, H. Li-hua, G. Shan, Z. Hui, Z. Jing-gui, and L. Ning, "Molecular orientation and gas-sensing properties of Langmuir-Blodgett films of copper phthalocyanine derivatives," *Sensors and Actuators B: Chemical*, vol. 126, no. 2, pp. 588-594, 2007.
- [141] A. K. Sharma, A. Mahajan, S. Kumar, A. K. Debnath, and D. K. Aswal, "Tailoring of the chlorine sensing properties of substituted metal phthalocyanines non-covalently anchored on single-walled carbon nanotubes," *RSC Adv.*, vol. 8, no. 57, pp. 32719-32730, 2018.
- [142] A. K. Sharma, A. Mahajan, R. K. Bedi, S. Kumar, A. K. Debnath, and D. K. Aswal, "Non-covalently anchored multi-walled carbon nanotubes with hexa-decafluorinated zinc phthalocyanine as ppb level chemiresistive chlorine sensor," *Applied Surface Science*, vol. 427, pp. 202-209, 2018.
- [143] A. K. Sharma, A. Mahajan, R. Saini et al., "Reversible and fast responding ppb level Cl_2 sensor based on noncovalent modified carbon nanotubes with hexadecafluorinated copper phthalocyanine," *Sensors Actuators, B Chem.*, vol. 255, pp. 87-99, 2018.
- [144] M. Passard, C. Maleysson, A. Pauly, S. Dogo, J. Germain, and J. Blanc, "Gas sensitivity of phthalocyanine thin films," *Sensors and Actuators B: Chemical*, vol. 19, no. 1-3, pp. 489-492, 1994.

- [145] R. Saini, A. Mahajan, R. K. Bedi, D. K. Aswal, and A. K. Debnath, "Room temperature ppb level Cl_2 detection and sensing mechanism of highly selective and sensitive phthalocyanine nanowires," *Sensors Actuators, B Chem.*, vol. 203, pp. 17–24, 2014.
- [146] S. Kumar, A. K. Sharma, M. K. Sohal et al., "Room temperature highly sensitive chlorine sensor based on reduced graphene oxide anchored with substituted copper phthalocyanine," *Sensors and Actuators B: Chemical*, vol. 327, p. 128925, 2021.
- [147] T. Watanabe, T. Idehara, Y. Yoshimura, and H. Nakazawa, "Simultaneous determination of chlorine dioxide and hypochlorite in water by high-performance liquid chromatography," *Journal of Chromatography A*, vol. 796, no. 2, pp. 397–400, 1998.
- [148] K. Wakigawa, A. Gohda, S. Fukushima, T. Mori, T. Niidome, and Y. Katayama, "Rapid and selective determination of free chlorine in aqueous solution using electrophilic addition to styrene by gas chromatography/mass spectrometry," *Talanta*, vol. 103, pp. 81–85, 2013.
- [149] T. Watanabe, K. Akai, and Y. Einaga, "The reduction behavior of free chlorine at boron-doped diamond electrodes," *Electrochemistry Communications*, vol. 70, pp. 18–22, 2016.
- [150] Y. Qin, H. J. Kwon, M. M. R. Howlader, and M. J. Deen, "Microfabricated electrochemical pH and free chlorine sensors for water quality monitoring: recent advances and research challenges," *RSC Advances*, vol. 5, no. 85, pp. 69086–69109, 2015.
- [151] T. Han, A. Nag, S. Chandra Mukhopadhyay, and Y. Xu, "Carbon nanotubes and its gas-sensing applications: a review," *Sensors Actuators, A Phys.*, vol. 291, pp. 107–143, 2019.
- [152] M. Zaki, U. Hashim, M. K. Arshad, and M. Nasir, "Characterization of difference carbon nanotube (CNTs) as a sensing mechanism for develop of formaldehyde gas detection sensor," in *IEEE Regional Symposium on Micro and Nanoelectronics (RSM)*, pp. 1–7, Penang, Malaysia, 2017.