

SENSOR BASED METHOD TO DETECT AND MONITOR H₂S GAS – A REVIEW

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ABSTRACT

This paper reviews work for sensor design along with sensing characteristics (stability, sensitivity, responsetime, range of operation etc.) to detect and control the risk of manure gas (H₂S gas). The comparison between sensors can be done on the basis of operating range of gas concentration and working principle and limitations of different parameters of sensor are identified. Solid state gas sensor measure intensive parameters on a successful scale and less successful in measuring concentration of gas (H₂O₂, CO, CO₂, methane etc). It was observed that sensing parameters can be explored for detecting H₂S gas by using semiconductor metal oxide such as CuO, SnO₂, ZnO, NiO, etc. Recently has been seen that CuO-based sensors have good sensing properties toward H₂S gas. The alternative of metal oxide sensor is use of conductive polymer on sensitizing surface. It is reviewed that ultrafast response/recovery and high selectivity parameters are very promising when hydrogen sulphide gas sensors are fabricated using α -Fe₂O₃ nano-ellipsoids. It also describes future aspects of these sensor based method.

KEY WORDS : H₂S, Detecting and monitoring H₂S, Air pollution

INTRODUCTION

Hydrogen sulfide gas is a common toxic gas which is released into environment mainly during the energy production process from coal and crude oil, its smell like rotten eggs which is referred as sewer gas or manure gas. Hydrogen sulphide gas is release when there is decay of organic matter and it can also occur when breakdown of bacteria occur (through wastage of human and animal). This gas is naturally produced in Kraft paper mills and also in refining of petroleum and landfills hydrogen sulphide gas is widely exists in many industrial processes, decomposition of organic material, natural gas and also in petroleum industry (Kim *et al.*, 2006; Kim *et al.*, 2008).

The effect of this gas is very harmful to our lives even at low concentration and it may cause death at high concentration (Kim *et al.*, 2006). When low concentration of hydrogen sulphide gas is exposed then it leads to health problem like eye injury, throat injury, poor memory and loss of reasoning and

balancing. This gas is responsible for many accidents in petroleum industry, gas industry and also in paper mills due to its toxic nature, its concentration and also due to duration of exposure.

Below Table shows that concentration of hydrogen sulphide gas and its effect on human body (Habeeb *et al.*, 2017) :

Sr.No	Concentration	Disease
1	2 ppm	Nausea
2	20 ppm	Loss of smell
3	100 ppm	Eye injury /throat injury / irritation
4	>250 ppm	Fatel death

Due to all of these disadvantages, it is very important to monitor and measure at proper time from environment there are many materials and various type of methods have been used for detecting H₂S gas (Pandey *et al.*, 2012). Sensor based on metal oxide, optical sensor and electrochemical sensors are used to monitor this gas there have been a rapidly growth in sensing technology.

Electrochemical sensor is the method for detecting H₂S gas along with electrochemical sensor, optical method/optical sensors are used. The principle of optical sensors based on fluorescence or direct optical detection in heterogeneous phase. Most of sensors has principle based on absorption and fluorescence (Guth *et al.*, 2009; Gauglitz, 2004).

From the last few decades, chromatography and spectrometry method are used to identify the H₂S concentration in environment but these method are not so popular because of their complex sampling, analyzing process and high fabrication cost (Zoccali *et al.*, 2019). Electrochemical and optical methods are of relatively high cost and implementation on gas sensor is restricted due to selectivity and limit temperature range. Researchers work on sensing properties and various type of sensors have been developed. These sensors become very popular because of its fabrication process and their excellent sensing performance. The sensor parameter like response time, recovery rate, high sensitivity, selectivity, stability etc. vary on the basis of design of fabrication of sensor, material type and on the principle involved in different sensors.

There are some promising materials which are used to detect H₂S gas. These material oxide-semiconductor material are used because of their properties. It is reviewed that in comparison of bulk structure, nonmaterial exhibit important properties or good sensing properties due to large surface area in comparison of volume. To increase the parametric performance of sensors, organic and inorganic materials are used for detection of H₂S gas (Rout *et al.*, 2008).

It is reviewed that these sensing parameters can be explored for detecting H₂S gas by using ZnO, CuO, MoO₃, NiO, SnO₂ and α -Fe₂O₃ nanostructure metal oxide. Among all of these, CuO and α -Fe₂O₃ nonmaterials are promising material on behalf of their non-toxicity, low cost and in detection of various types of gas (ethanol, acetone, trimethylamine, NH₃ and H₂S) and show excellent sensing performance for H₂S (Diao *et al.*, 2016). It was noted that the sensing parameters can vary with size, morphology and porosity of α -Fe₂O₃. The concentration of H₂S gas at ppb level will be achieved by using Fe₂O₃ nanostructure. The sensing parameter's performance can be further increase when Fe₂O₃ is modified by using Nobel metals (Yan Wang *et al.*, 2008).

H₂S gas sensor based on α -Fe₂O₃ nanoellipsoids (formed by hydrothermal method) show ultrafast

response (0.8s to 2.2s), good recovery rate and excellent selectivity toward H₂S gas. Recently metal oxides appear as excellent sensitive material specially in hydrogen sulphide sensing. CuO based H₂S sensor use a narrow band gap semiconductor CuO which gave good response to H₂S gas. These sensors has excellent selectivity and sensitivity towards H₂S gas (Choi *et al.*, 2013; Chen *et al.*, 2008). The sensor based on metal oxides has high sensitivity, fast response, easy fabrication but limited selectivity and high dependence on relative humidity and also has high operating temperature (> 100 °C). It is review that there is alternative of metal oxide sensor that is use of conductive polymer on sensitizing surface (Duc *et al.*, 2020).

In this review, firstly sensors are discussed on basis of principle and then on material type. Most promising hydrogen sulphide gas sensing method is to be identified and discuss them along with their advantage, drawback and future perspective.

MOST COMMON SENSOR'S TYPES USED IN ANALYSIS OF H₂S

The development in search of new materials for H₂S sensors is because of compelling demand for low power consumption, low limit of detection and because of their low cost. In this review, for monitoring H₂S gas, important and common techniques in sensors have to be reported. Different types of sensor based on the material used and also on the working principle. These sensors are discussed below:

ELECTROCHEMICAL SENSOR

Electrochemical sensing technology began in 1950s for detecting oxygen gas and this technology became popular till 1980s because of the reason that these sensors can detect and measure the toxic gas from environment especially hydrogen sulphide. These type of sensors are based on electrolyte (may be solid or liquid electrolytes). This sensor operates when electric signal is produced via interaction of gases, the production of signal is based on the concentration of gas. On the basis of electrolyte, there are two type of electrolyte sensor (solid and liquid electrolyte), further divide electrochemical sensor into two type of sensors based on the basis of working principle, i.e. amperometric and potentiometric.

Amperometric sensors used to produce current

signal and its rate of production of current signal is based on the concentration of analyte. These type of sensors are used to monitor the different gas such as CO, NO₂, O₂, glucose etc. Because of reliable properties, liquid electrolyte electrochemical cell is used in the detection of H₂S gas. Solid electrolyte sensors (solid polymer electrolyte –SPE) are used in determination of gas phase for H₂S in laboratory conditions. It showed a great performance over seven months with concentration of 100 ppm H₂S gas for 4hr per day. It was observed that the performance of sensor gets reduced because of the deposition of sulphur.

Potentiometric sensors produce potential signal by using ion electrode and rate of production is logarithmically proportional to concentration. This sensor is used to detect H₂S gas and its capacity for detection is 5-50 ppm with response time 4-8s. The selectivity of sensor towards H₂S have been improved by using Au catalyst as an alternative electrode (Scozzari, 2008).

It is reviewed that solid electrolyte sensor suffer from a number of limitation in sensing parameters because of intensive parameters, short life and low performance in composition of H₂S gas.

OPTICAL SENSOR

In the early of 1977s, parameter like pressure, temperature, magnetic field and electric current are sensed by optical sensors. The most effective chemical sensor is optical sensor which is based on the attenuation of light wave (Toda *et al.*, 2004). The fabrication of these sensors depends on light interaction with analyte which is placed at interface of fiber/coating and can monitor the response via absorption and emission spectroscopy. These type of sensors can record excellent performance in stability and monitoring even at harsh environment. There are two types of sensing techniques are involved (direct and indirect) in optical sensor. Direct sensing technique such as IR, FTIR, UV absorption etc, analyte is detected through intrinsic optical property (Varga *et al.*, 2006). Indirect sensing technique requires the reagent (solid/liquid) for analysis of detection of H₂S gas. To operate this sensor for 8hr, 1ml of reagent is necessary.

It is reviewed that WENS (wireless electronic nose system) was designed to quantify H₂S and NH₃ along with their mixture. Various efforts have been initiated for a simple, fast response, low cost optical method to monitor the H₂S gas in concentration of

50 ppb- 50 ppm (Sen *et al.*, 2008). This method became popular because of its operating temperature (Jiang *et al.*, 2013).

SOLID STATE GAS SENSOR

These sensors are of three types based on sensing principle.

- (1) Solid Electrolyte Gas Sensors- These sensors are useful in high ionic conductivity at high temperature range 773 to 1573 K. The working principle of these type sensors is that oxygen ion conductor (Zirconia) act as solid electrolyte and have different oxygen potentials for separating two compartments with gaseous mixture working on this principle, oxygen sensors has wide application in combustion control in heat treatment furnaces, glass tank furnace, oil and gas stoves, boilers and oxygen control in melting of metals such as steel, copper etc. It is reviewed that due to quick monitoring, accuracy, simple design wide range of composition of zirconia, these sensors are very advantageous.
- (2) Catalytic Combustion Sensors:- It is a single port device in which sensing material act as heater. These types of sensors are fabricated with mounting bead in platinum coil (highly dispersed catalyst). The combustion gas reacts with the catalyst and burn on the Pt. coil. The target gas can rise the temperature of element up to 673-723 K.

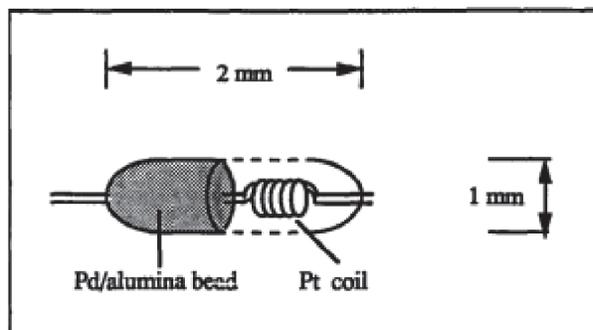


Fig. 1. Structure of catalytic combustion sensor element) (Azad *et al.*, 1992)

- (3) Semiconductor Gas Sensors: - These sensors are widely used for detection of various gases from explosive gases (propane), toxic gases such as carbon monoxide. Mostly used semiconductor gas sensors are metal oxide semiconductor gas sensors (Cobianu *et al.*, 2016). The metal oxide gas sensor technology is based on change in

resistance of sensitive metal oxide layer on metal oxide which depends on the interaction of absorbed oxygen with gas, working temp. Range, grain size. The sensing material may be in form of heater or semiconducting material. This type of sensors achieves high level of selectivity based on the suitable coating. Detection limit is depend on the type of material used. Working principle is based on absorption/disabsorption of the gas on metal oxide will change its conductivity and resistivity. Thus change in detection of target gas either change in conductivity or resistivity.

METAL OXIDE SEMICONDUCTOR MATERIAL BASED SENSORS

Sensor based on metal oxide such as Zn, Sn, Cu etc are very promising sensor because of the excellent characteristics (size, cost, power consumption) of metal oxide. When any gas is exposed on metal oxide then electronic properties gets change which show change in sensing system (Wang *et al.*, 2010). Due to their fast response and ability of detection of H₂S at room temperature and low concentration, these materials are widely used. SnO₂ is mostly used in detection of H₂S gas at room temperature in range of 1-15ppm having recovery time of 40s and response time of 20s (Kanan *et al.*, 2009). The response toward H₂S gas can be changed by changing the film thickness (by decreasing the film thickness response time can be increase). The sensitivity of sensor can be increase by using Ag as do-pant because Ag₂O particles are at grain boundaries of SnO₂ and there is p-n hetro-junction formed (Gong *et al.*, 2006). When Fe doped SnO₂ is used then H₂S gas can be detected in the range of 10-250 ppm having response time of 5-15s. Fe₂O₃ based sensors were found to be highly selective for target gas (100ppm for 100hr) (Vaishampayan *et.al.*, 2008). Tanda *et al.* (2007) used ZnO semiconductor sensor for detecting H₂S gas (Tanda *et al.*, 2007). The use of nanostructures material improve the gas sensing property.

It is reviewed that CuO is used to promote the sensing properties of SnO₂. When CuO is used then sensor exhibit sensitivity in the range of 20 ppm and response time is 15s. In detection of low level H₂S gas, SnO₂-CuO sensors were fabricated on silicon substrate. It was studied that CuO modified SnO₂ films were able to detect H₂S in 1-1200 ppm concentration range with response time of 15s. H₂S

sensor based on metal oxide semiconductor was found highly sensitive and selective toward this gas.

It was studied that iron molybdate has good potential when it is used as sensing material. It was observed that Pd modified sensor showed a good response toward H₂S gas. The improvement in sensing parameter could not have been possible without some semiconductor material and catalyst. N-type oxide semiconductor increases the result of H₂S gas sensor. Along with n-type, Wo₃ has gained more attention towards detection and sensitivity of H₂S (Hübner *et al.*, 2011).

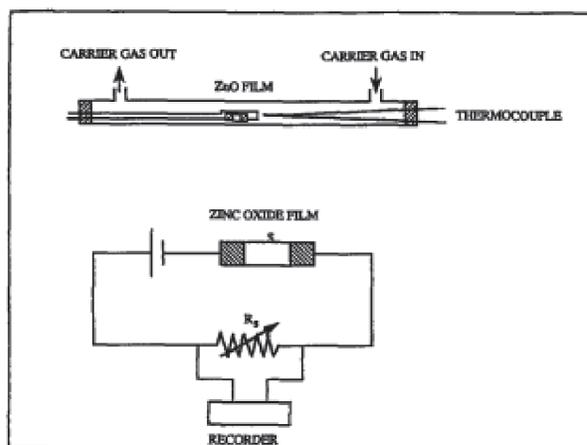


Fig. 2. (ZnO based semiconductor sensor) (T. Seiyama *et al.*, 1962)

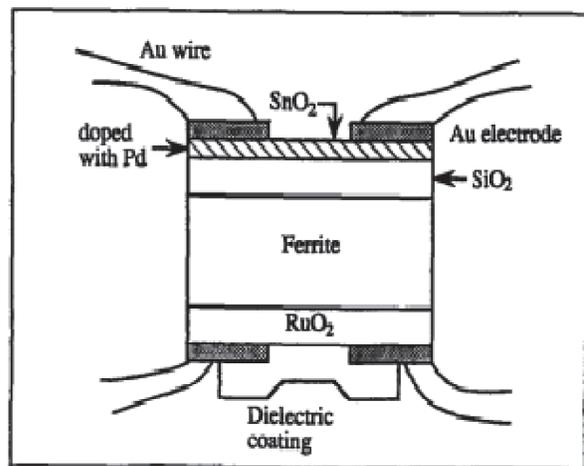


Fig. 3. (SnO₂ based semiconductor sensor) (Azad *et al.*, 1992)

ORGANIC-INORGANIC BASED SENSORS:

The fabrications of electronic device based on organic and inorganic materials gain so much interest because of their properties of size, power saving and portability. Due to structure, size,

morphology, active surface area, $W\text{o}_3$ nanostructure sensor detects H_2S gas at very low concentration (Jiang *et al.*, 1998).

SENSORS BASED ON CONDUCTIVE POLYMERS

Chemiresistive sensors based on CP (conductive polymer) are a good sensor in comparison of electrochemical and optical sensors because of their simple designing, low cost and in term of performance (Duc *et al.*, 2020). The most common approach for increasing the sensing performance is that to hybridize them with noble metal particles, metal oxide and carbon based nano-objects (called as inorganic fillers) (Park *et al.*, 2017). When these fillers are added then limit of detection and response time decrease which leads competing it to the metal oxide sensors. These sensors can easily be tuned by changing monomer and dopants and CP showed a great potential in H_2S sensing application (Dong *et al.*, 1889).

CONCLUSION

Excellent sensing technology for hazardous hydrogen sulphide gas because of its toxic nature and act as pollutant have been reviewed. It is reported that most common sensors are electrochemical sensor, optical sensor, metal-oxide semiconductor sensor, nano-structured material based sensor, inorganic and organic material based sensors, conductive polymer based sensor. Gas sensor can be divided into three categories (1) semiconductor sensor (2) catalytic combustion sensor (3) solid electrolyte sensors.

In electrochemical sensor, solid polymer electrolyte is commonly used because of its low cost, small size and limit of detection. In optical method, direct sensing technology has great potential for monitoring H_2S gas. In form of sensor array system (WENS), the sensing material can improve the monitoring range up to ppb level. It is also reviewed that n-type metal oxide sensors because of their advantage (low cost and high sensitivity) are mostly used. Based on organic and inorganic nano composite, gas sensing parameters have shown good response.

It is reviewed that mostly sensors are operated under laboratory conditions and it is further need to validate in harsh environmental conditions. There are major factor such as stability, cost response time

which must be taken into account in fabrication of H_2S sensors. In designing of reliable instrumentation, it is require resolving problem of poor delectability, selectivity and understanding of mechanism. One of the major issues for practical application of H_2S gas sensor is cost which can be resolved by using metal oxide based sensors but these sensors suffer from poor selectivity in presence of humidity.

It is observed that for increasing sensing performance, conductive polymer hybridized with inorganic fillers (noble metal particle, carbon based nano object) and these sensors can easily tuned by changing monomer and do pant, CP showed great potential in H_2S sensing application. It is reviewed that of $\alpha\text{-Fe}_2\text{O}_3$ nano ellipsoid based gas sensor show excellent H_2S gas sensing characteristics (fast response/recovery speed, good selectivity and range of detection). However it is more to be investigating the link between material properties and sensing performance of gas sensors. For future perspectives, new materials are to be investigated for achieving high selectivity, high sensitivity, low detection range, small size and low cost.

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