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HYDROGEN SULPHIDE SENSING REVIEW

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Abstract. *This paper reviews few of the most commonly employed sensing structures for hydrogen sulphide detection. Categories of sensors such as semiconductor metal oxide, electrochemical, optical (including colorimetric), conducting polymers, piezoelectric (including quartz crystal microbalance and surface acoustic wave) are discussed in terms of principles, materials used as sensing layers and performance.*

Keywords: Sensors, Dosimeter, Hydrogen Sulphide, Metal Oxide Semiconductor, Colorimetric, Surface Acoustic Wave

1. Introduction

Hydrogen sulphide (H_2S) is a flammable, irritating, corrosive, typically bad-smelling and extremely toxic gas. The toxicity of H_2S is comparable with that of hydrogen cyanide, which is considered a broad-spectrum poison. At concentrations higher than a few ppm in air, H_2S is a very toxic gas for people, with harmful effects on respiratory and nervous system. Actually, its maximum threshold limit value (TLV) is 1 ppm for eight-hour a day exposure, while short term exposure limit (STEL) is 5 ppm, but these values, as imposed by international regulations and legislation, are decreasing every year. This explains the strong health safety environment (HSE) regulations for monitoring this gas in all industrial areas where this may be present. H_2S is generated by oil and gas industry during crude oil extraction, its refinement and transportation, as well as by the decay of organic matter in septic sewers systems [1]. In North America only, well over 150,000 workers are exposed or potentially exposed to H_2S every year. Thus, it is of crucial importance to permanently monitor the H_2S level and provide safeguards for the employees who work in refineries and petrochemical plants.

The detection of the H_2S can be performed by means of either chemo-resistive, electrochemical (amperometric or potentiometric), conducting polymers, optical (including colorimetric) or piezoelectric principles. The first two approaches have been available at commercial level for about five decades.

2. Common sensors types employed for H_2S sensing

For the detection of hydrogen sulphide, chemical, electrochemical and physical principles have been used, so far. In this chapter, the latest data regarding material and device research for increasing the stability, sensitivity and accuracy of such sensing structures will be presented.

2.1 Semiconducting metal-oxide sensors

The research on miniaturized metal-oxide semiconductor (MOX) H_2S sensors has attracted a great interest due to certain advantages like simple manufacturing process, compatibility with integrated circuits (IC's) and microelectromechanical systems (MEMS) technologies, low cost, small size and low electric power consumption. The most frequently used chemo-resistive sensor is based on thin or thick layers of metal-oxide and incorporates a low power heater. When exposed to H_2S, the metal-oxide layer changes its electronic properties such that the electrical resistance of the MOX layer decreases, as H_2S concentration increases.

Figaro, Simtronics, Mil-Ram Technology, Detcon are some of the companies that commercialize MOX-based H_2S sensors. Unfortunately, these commercially-available sensors are either not able to measure H_2S at concentrations below 5 ppm (e.g., Taguchi 825 produced by Figaro), or lack good accuracy at H_2S level near TLV (accuracy of +/-2 ppm). In addition, they all exhibit large electric power consumption levels (above 0.6 W), which drastically limits the autonomy of battery-powered portable gas detection instruments.

The most widely used metal-oxide is SnO_2, either as thin or thick film, either pure or doped with materials such as CeO, Pd, Ag, CuO, ZnO, MoO_3, NiO [1, 2]. Among these various dopants, CuO seems to be very efficient in enhancing H_2S sensing properties of SnO_2 [3]. The increased sensitivity of the CuO - SnO_2 sensor is due to the formation of a p-n junction at the interface of these materials and on its subsequent disappearance due to the conversion of CuO in metallic CuS when reacting with H_2S [3]. Using a SnO_2 - CuO sensor, an H_2S concentration as low as 100 ppb was detected [4]. H_2S concentrations below 1 ppm were detected by structures based on SnO_2 doped with MoO_3 and NiO [2].

Other materials, such as WO_3, ZnO and In_2O_3, were also used, especially nano-structured for H_2S detection. Such nanomaterials have great potential for improving the sensitivity toward gas detection due to the large interface between the oxide and gas given by a large surface area of the metal oxide. For instance, a WO_3 nanoparticles based sensor was able to detect H_2S at concentrations of 20 ppb [5]. ZnO nanorods were also used for detection of 50 ppb H_2S [6]. Finally, In_2O_3 whiskers-based sensors were able to detect concentrations of 200 ppb H_2S gas [7].

2.2 Conducting polymers-sensors

Conducting polymers based sensors have been also investigated for H_2S detection [1]. Typically, these sensors use a mixture of conducting materials (like carbon nanotubes - CNTs) and polymers that form a composite sensing material. The sensing mechanism is based on the change in the resistance of the composites. This happens because the polymers swell when reacting with the gas and break

some of the conductive paths of the conductive material network. Different composite materials such as metal salts-polyaniline nanofibers and polyaniline nanowires-gold nanoparticles were investigated for H_2S sensing [1]. A low detection limit of 0.1 ppb was achieved by employing the polyaniline nanowires-gold nanoparticles hybrid network [8].

Polyaniline (PANI) nanofibers-based composites, containing metal salts such as $CuCl_2$, $ZnCl_2$, and $CdCl_2$, exhibit an enhanced response to hydrogen sulphide when compared to simple PANI [9]. Such a PANI-metal chloride mixture behaves like a base-PANI and shows very low electric conductivity. The sensing mechanism is based on the increase in conductivity of the sensing film due to the reaction between the metal salt and H_2S:

$$CdCl_2 + H_2S = CdS + 2HCl \quad (1)$$

The product of this reaction is the hydrochloric acid (a strong acid), which reacts with base-PANI (**Fig. 1**) by protonating it. Thus, a salt emeraldine is obtained (**Fig. 2**), which explains the increase of conductivity of the film in the presence of the H_2S.

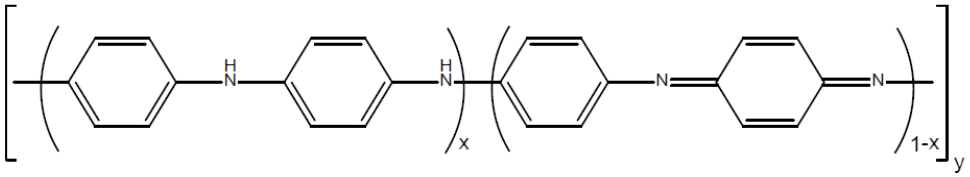

Fig. 1. The structure of emeraldine base.

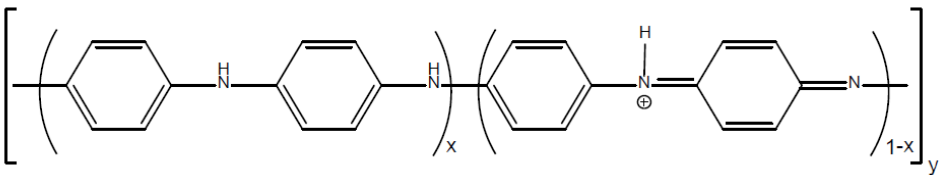

Fig. 2. The structure of emeraldine salt.

The sensor manufacturing process starts from a solid substrate such as SiO_2/Si, quartz, glass, etc., on which metallic interdigitated electrodes (IDEs) and sensing layers are subsequently deposited by different direct printing techniques. As described below, in case the metallic electrodes do not react with the incorporated metal salt, a disposable sensor or a dosimeter is obtained; while when the metal electrodes do react with the metal salt, a sensor is produced.

The increase of the sensing film conductivity is correlated with the concentration of H_2S. As a result of the reaction of H_2S with the PANI-metal salt nanocomposite, one obtains metal sulphide and conducting emeraldine salt.

Both are irreversible products in the presence of carbon paste IDEs. Such irreversible products do not allow the recovery of sensor in the absence of H_2S, and therefore an H_2S dosimeter is obtained for a carbon IDEs-PANI-metal salt device configuration.

On the other hand, a structure comprising PANI-$CuCl_2$ and Ag IDEs acts as a sensor due to the reaction between $CuCl_2$ and Ag which leads to solid Cu and AgCl. Both solid Cu and AgCl are further reacting with H_2S generating reaction products such as HCl, protons and electrons [10]. Obviously, as long as solid copper and AgCl are created by the above mentioned mechanism, they will react with H_2S, thus increasing the conductivity of the sensing layer. At the same time, the same conductivity will decrease in the absence of H_2S.

The detection of H_2S at elevated temperature requires polymers with high thermal stability. Mixtures of PANI and isolator polymers (such as polyvinyl chloride) show improved behavior at elevated temperatures (150-200^{0}C) in comparison with simple PANI [11]. At the same time, nanocomposites comprising PANI and clay also show improved behavior at elevated temperatures (150-200^{0}C) in comparison with simple PANI [12].

For H_2S detection at elevated temperature (150-200^{0}C), we have proposed two types of matrix nanocomposites sensing structures [13]:

1. Polyaniline / isolator polymer / silver (I) or copper (I) salts;
2. Polyanilines / clay/ silver (I) or copper (I) salts.

The PANI nanofibers can be obtained from interfacial polymerization of *o*-methoxy or *o*-ethoxy aniline. The isolator polymers can be polyvinyl acetate, polystyrene or polyvinyl chloride. The selected clays include muscovite, kaolinite, montmorilonite and dickite.

It is important to mention that the sensing mechanism described above is in excellent agreement with the HSAB (Hard Soft Acid Base) principle. H_2S, which is a soft base, has a strong interaction with cations like Cu^+, Ag^+, Hg^{2+} , classified as soft acids:

$$2Cu^+ + H_2S = Cu_2S \downarrow + 2H^+ \quad (2)$$

$$2Ag^+ + H_2S = Ag_2S \downarrow + 2H^+ \quad (3)$$

2.3 Electrochemical sensors

Among companies producing electrochemical H_2S sensors, one can mention City Technology (owned by Honeywell) and Alphasense. The detection process employed by such structures is either based on the amperometric principle (electrical current variation in an electrode is proportional with the

H_2S concentration) or on the potentiometric principle (electrical potential of an electrode varies with the H_2S concentration). Among amperometric sensors, an H_2SO_4 pre-treated Nafion® membrane using Au as catalyst was found to be able to detect 0.1 ppm of H_2S [14]. A potentiometric sensor based on NASICON and Pr_6 O_{11}-doped SnO_2 was able to measure H_2S in the 5-50 ppm range [15]. However, electrochemical H_2S sensors have major limitations mainly related to potential liquid electrolyte leaks and to the fact that they are bulky, which makes them unsuitable for the next generation of portable gas detectors.

2.4 Optical sensors

The optical sensors are another type of sensors investigated for H_2S detection, employing both direct sensing and indirect (reagent mediated) approaches. Several types of indirect (reagent mediated) optical sensors such as colorimetric or micro-fluorescence based were developed for H_2S detection with promising results [1].

An H_2S sensing layer based on mixtures of dextran (**Fig. 3**) and an iron (II) salt (such as ferrous chloride or ferrous acetate) was proposed [16]. This type of colorimetric sensor has the following advantages:

- The sensing layer comprises only two elements;
- It is environmentally friendly and biodegradable;
- It is based on a single chemical reaction;
- It is based on the excellent compatibility between iron cations and dextran (solutions based on the iron-dextran link are already commercially available and used in medical applications);
- No performance alteration due to relative humidity;
- No cross-sensitivity with other gases;
- Fast response time.

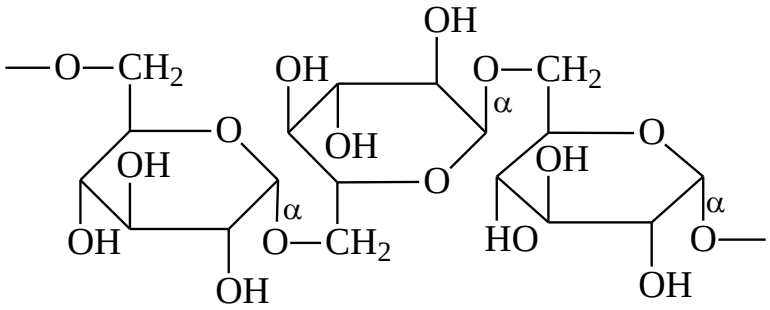

Fig. 3. The structure of dextran.

The color change observed when a target gas gets in contact with the substrate comprising dextran and an iron salt is proportional to the concentration of target gas (e.g., hydrogen sulphide) in the atmospheric gas drawn into the system.

For example, dextran iron (II) solution is brown, but when exposed to H_2S it leads to FeS which is a black compound. The system may be calibrated such that variations in the color change may be correlated to specific concentrations, or concentration ranges, of the target gas.

H_2S detection employing optical direct sensing approaches was also demonstrated. For instance, a fiber–optic evanescent-field laser sensor based on an uncoated fused-silica multi-mode fiber as sensor material and a single-mode distributed feedback laser (DFB) diode operating at 1.5705 μm as light source was developed for detection of H_2S, CO_2 and H_2O in the gas streams of a volcano [17].

Also, a direct optical detection of H_2S using wavelength-modulation spectroscopy and harmonic detection was reported by Weldon et al. [18]. They employed a DFB laser diode operating at 1.575 μm and thus they have obtained an H_2S detection limit below 10 ppm. A dual-channel H_2S sensor based on photoacoustic spectroscopy and built using a single-mode telecommunication-type laser diode operating at 1.5745 μm was developed by Varga et al. [19], thus H_2S detection at concentration levels as 500 ppbv was obtained.

2.5 Piezoelectric sensors

There are two types of piezoelectric sensors employed for H_2S detection: based on surface acoustic wave (SAW) effect and on quartz-crystal microbalance (QCM), respectively.

Both devices are based on the mass-change sensing principle [20]. Promising results were obtained with SAW sensors using WO_3 [21, 22], SnO_2/CuO [23] and nano-structured SnO_2 as sensitive films.

Such thin films exhibit good sensitivity to H_2S, but unfortunately the temperature required for sensing is still high (i.e. around 130^{o}C), thus leading to the employment of a heater.

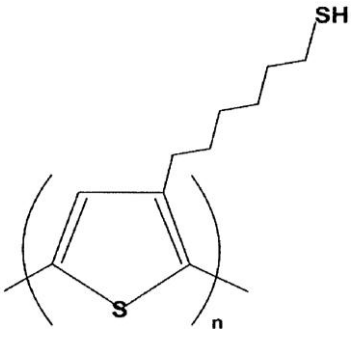

Fig. 4. The structure of poly[3-(6-mercaptohexyl) thiophene.

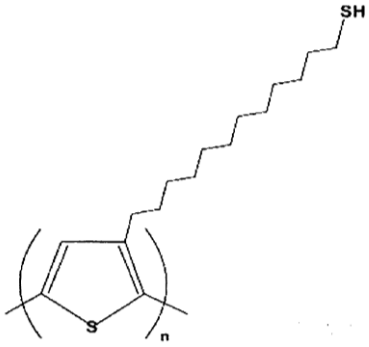

Fig. 5. The structure of poly[3-(12-mercaptododecyl) thiophene.

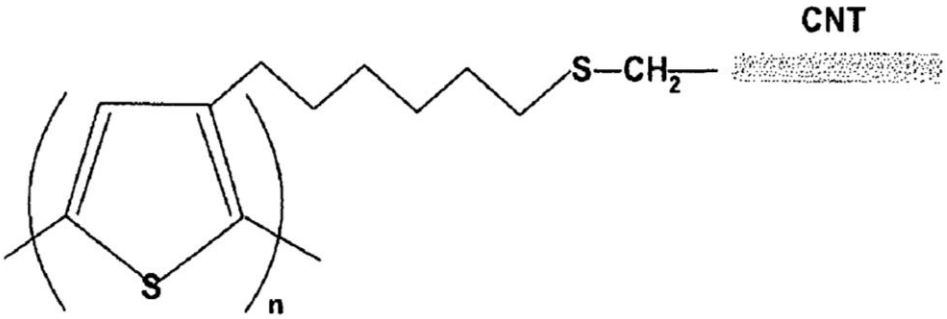

Fig. 6. Poly[3-(6-mercaptohexyl) thiophene functionalized with methylene CNTs.

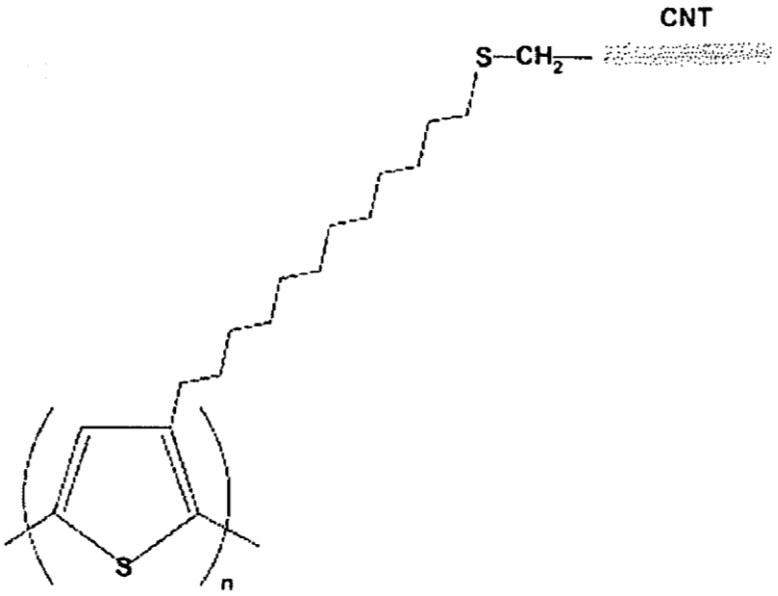

Fig.7. Poly[3-(12-mercaptododecyl) thiophene functionalized with methylene CNTs.

Functionalized carbon nanotubes, such as CNT-CH_2-SH, CNT-CO-NH-CH_2-SH, CNT- CH_2-S-CS-CNT, are also used in the SAW detection of H_2S [24]. In order to form matrix nanocomposites with improved mechanical properties, thiolated CNTs and networks of thiolated CNTs were incorporated into polymeric materials, such as poly[3-(6-mercaptohexyl) thiophene (**Fig. 4**), poly[3-(12-mercaptododecyl) thiophene (**Fig. 5**), poly[3-(6-mercaptohexyl) thiophene functionalized with methylene CNTs (**Fig. 6**), poly[3-(12-mercaptododecyl) thiophene functionalized with methylene CNTs (**Fig. 7**), or nanocrystalline WO_3 ceramic.

The flow diagram of the process employed for preparing an H_2S sensitive matrix nanocomposite is presented in **Fig. 8**:

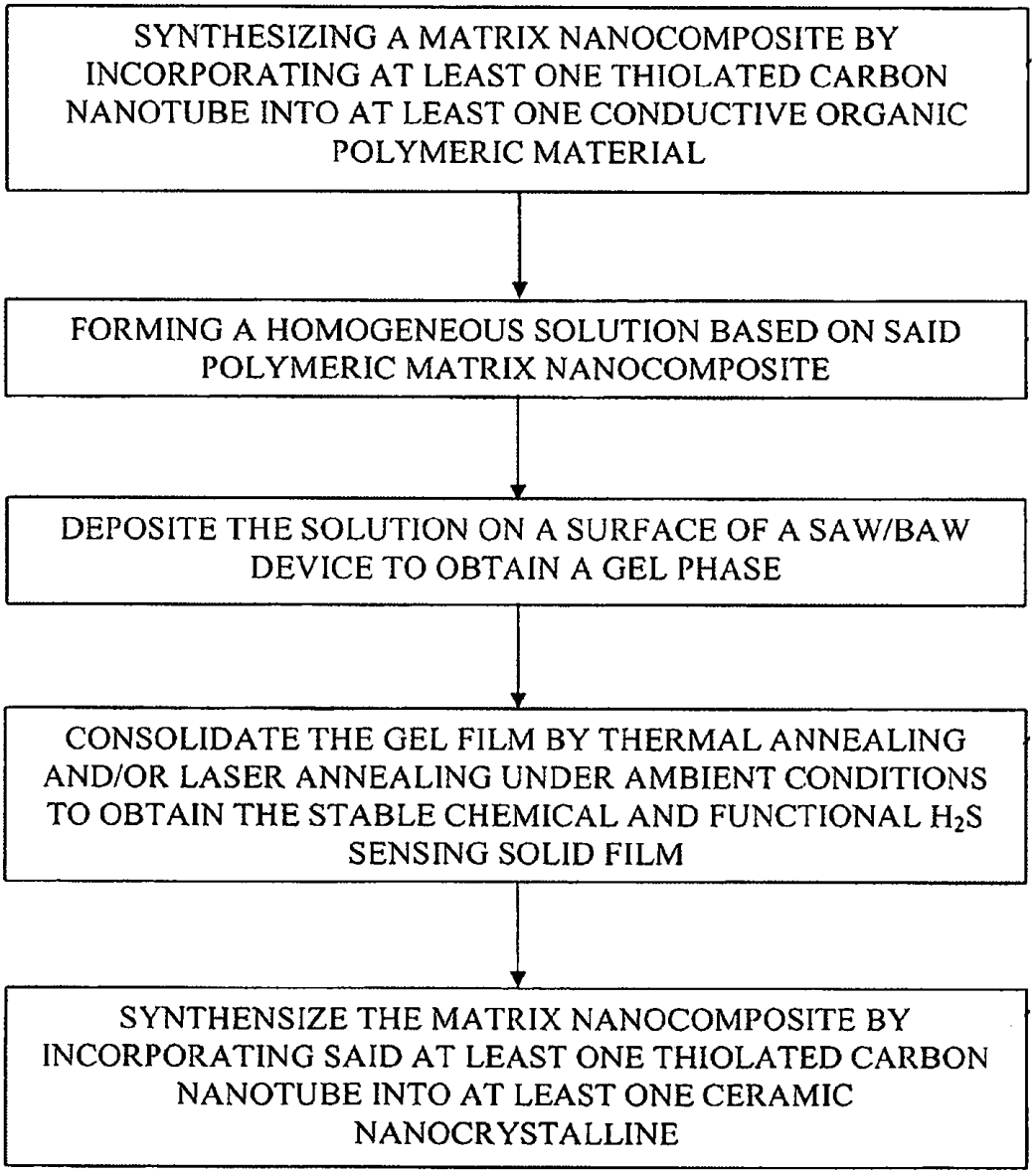

Fig. 8. The flow diagram of the method for preparing an H_2S sensitive matrix nanocomposite.

Recently, sensitive monolayers directly immobilized or anchored at the surface of piezoelectric quartz were proposed as a new solution for the detection of H_2S at room temperature [25]. The sensitive monolayer can be synthesized based on chemical compounds, which belong to one of the following classes of materials: thiacalix[n]arenes (**Fig. 9** – where n can be 4, 6, 8), mercapto halides (**Fig. 10**), chloromethylated thiacalix[4]arene (**Fig. 11**), mercapto alcohols (**Fig. 12**).

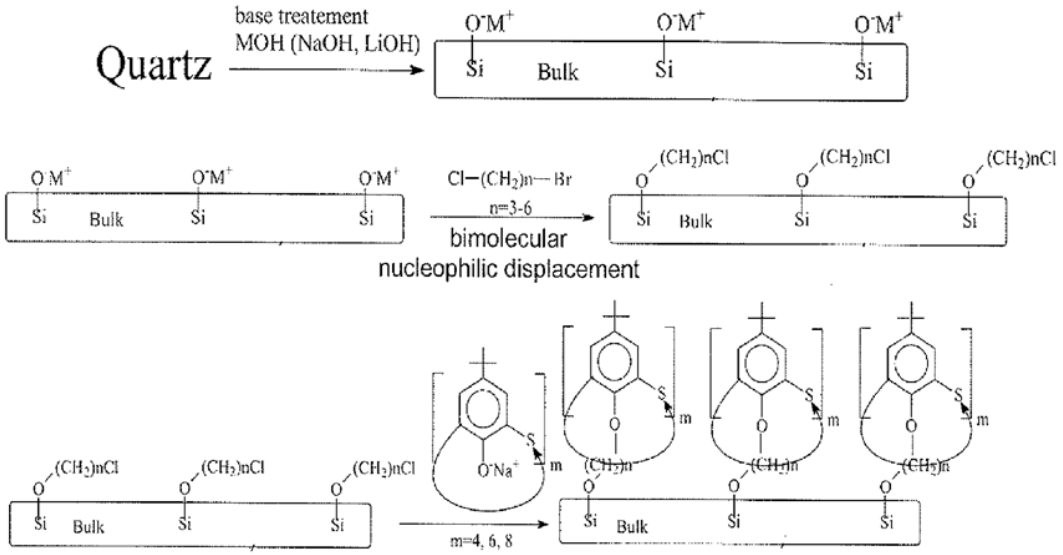

Fig. 9. Schematic diagram of a process employed for the on-chip immobilization of p-terbutylthiacalix[4]arene at the surface of a piezoelectric quartz substrate.

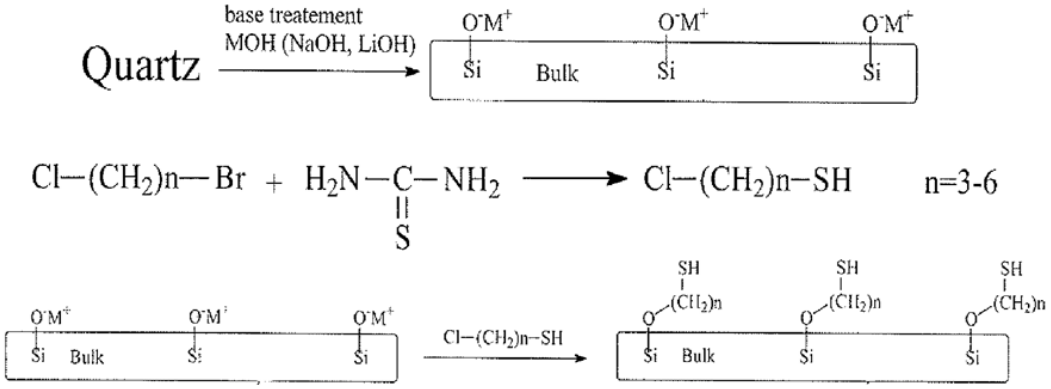

Fig. 10. Schematic diagram of a process employed for the on–chip immobilization of mercapto halides at the surface of a piezoelectric quartz substrate.

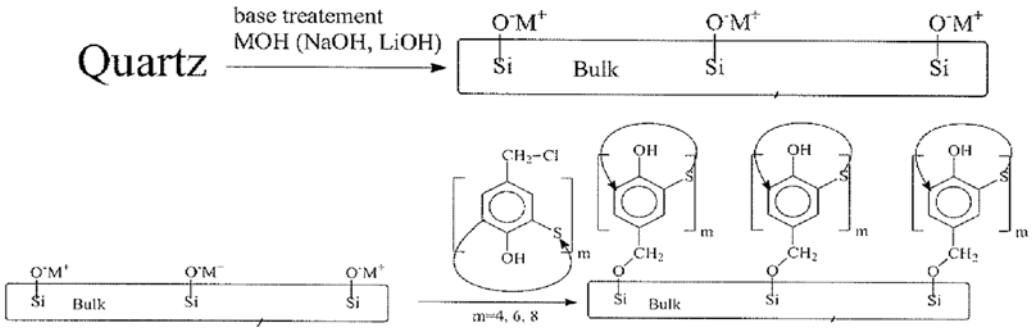

Fig. 11. Schematic diagram of a process employed for the on-chip immobilization of chloromethylated thiacalix[4]arene at the surface of a piezoelectric quartz substrate.

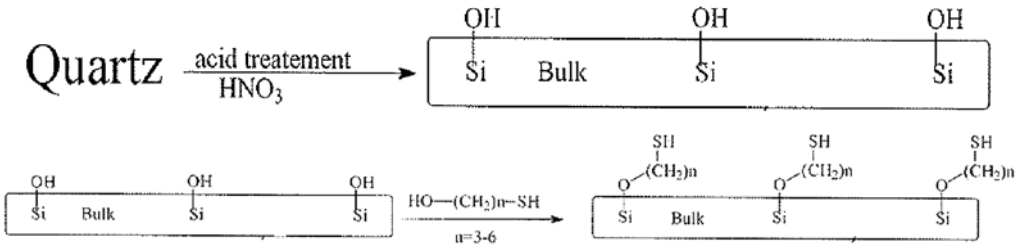

Fig. 12. Schematic diagram of a process employed for the on-chip immobilization of mercapto alcohols at the surface of a piezoelectric quartz substrate.

A flowchart of a method employed for designing the H_2S sensing monolayer at the surface of a piezoelectric quartz substrate is presented in **Fig. 13**.

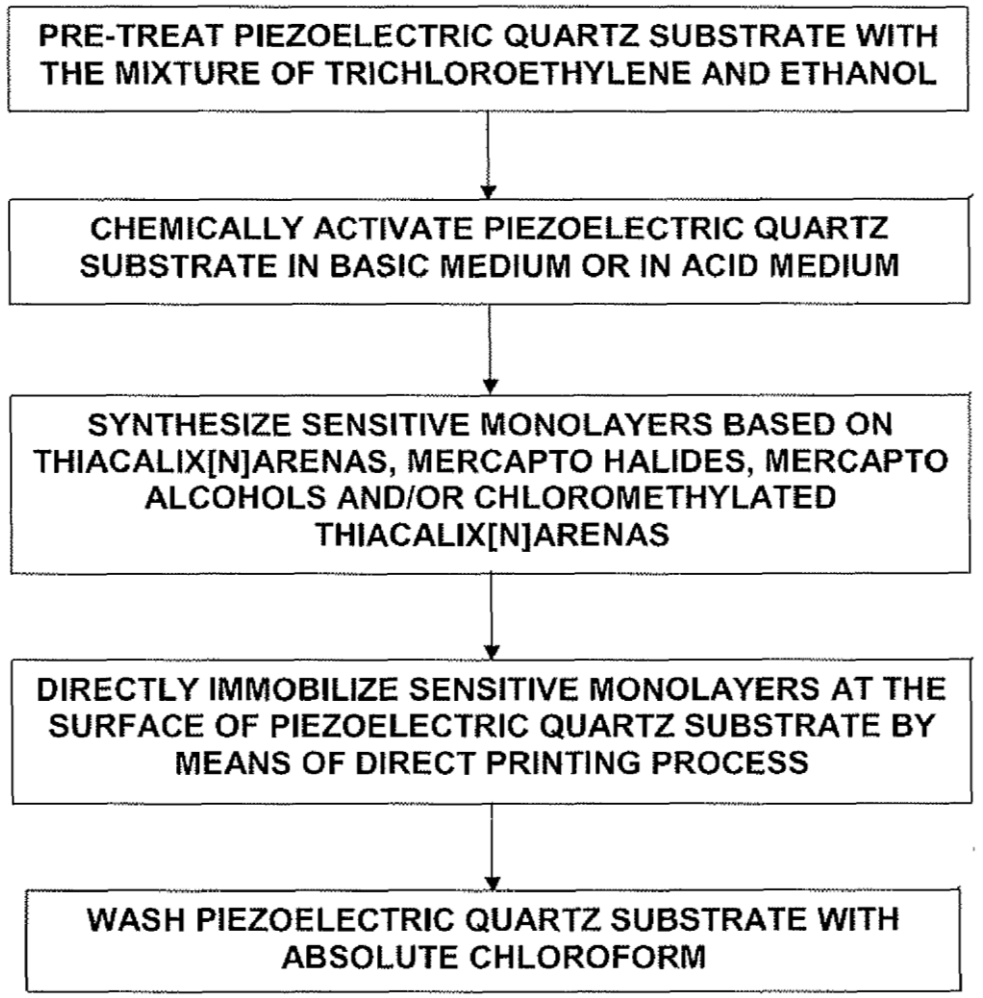

Fig. 13. Flowchart of a method for designing an H_2S sensing monolayer at the surface of a piezoelectric quartz substrate.

3. Conclusions and Future Prospects

Hydrogen sulphide is one of the key pollutants, due to its high toxicity and widely spread occurrence. In the last decades, many efforts have been devoted to finding a low cost, highly sensitive and robust solution for H_2S sensing. Several types of principles and methods for H_2S detection were presented in this review. Categories of sensors, such as semiconductor metal oxide, electrochemical, optical (including colorimetric), conducting polymers, piezoelectric (including quartz crystal microbalance and surface acoustic wave) were discussed in terms of sensing principles, materials used as sensing layers and performances.

Considering the above overview on the existing research trends in H_2S gas sensing and the societal trends towards real-time on-line monitoring of industrial processes and environment, it is our belief that low power-low cost, IC micro- and nano-technology compatible gas sensor will be the future of this domain. The early stage experimental results measured on gas sensors based on MOX nanostructured materials have shown remarkable sensitivity levels, low power consumption and compatibility with MEMS technology. The highest challenge for the next generation of MOX-based gas sensors is the control of sensing layer nano-structure, so that ultrahigh surface area and associated porosity is obtained with good repeatability. For this reason, the research community is currently developing new material synthesis methods based on deep understanding of the physical and chemical phenomena involved in processes such as (electro) spray pyrolysis, hydrothermal and sonochemical methods [26], all targeting hierarchically organized microstructures composed of nano-building blocks able to remain stable at the sensor operating temperature.

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