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GRAPHENE-BASED NANOSENSORS FOR HYDROGEN SULFIDE DETECTION: A SYSTEMATIC REVIEW

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Abstract: Hydrogen sulfide gases emit an unpleasant, toxic, corrosive and extremely volatile odor for both living organisms and the environment. One of the major challenges encountered in hydrogen sulfide detection has been to offer a fast, highly sensitive and affordable technique for monitoring these toxic gases. This gas is extremely harmful to both living organisms and the environment and, depending on its concentrations, can result in chronic diseases, worsen pre-existing conditions and, in more severe cases, result in death within minutes of exposure. Hydrogen Sulfide can be found in oil and gas extraction platforms, coal manufacturing, among others. Thus, this systematic review seeks to present specific studies to identify this gas through experimental analyses, simulations and computational calculations. For this, the search for articles was performed using four search platforms, *SienceDirect, PubMed, IEEE Xplore* and *Scopus*. There were no exclusion criteria regarding the year of publication. Of the 32 articles selected, only eight (8) were used to prepare this review. Taking into account this low number of selected articles, it is possible to affirm that it is necessary to develop more research involving the study, design, manufacture and use of prototypes for the monitoring of toxic gases.
Keywords: Nanosensor, graphene, detection, hydrogen sulfide.

INTRODUCTION

Hydrogen Sulfide (H2S) is a gas that emits an unpleasant odor, with a high degree of lethality, volatile, flammable and corrosive [1]. Its oxidation in the atmosphere results in the formation of acid rain, whose acidity harms lakes and, consequently, aquatic life, destroying vegetation and removing nutrients from the soil. Denser than air, this gas is usually found in oil extraction and in the decomposition of organic material. In addition, it is a highly toxic compound that can severely harm both living organisms and industrial production [2].

The severity of H2S to organisms will depend on the amount and duration of exposure, for example, about 300 ppm (μg g-1) for 30 minutes is enough to put a worker in a coma [3]. In some cases, this exposure can affect the nervous system, causing loss of consciousness [4]. In addition to these, the inhalation of sulfur can cause irritation to the respiratory membranes and tissues, generating inflammation, irritation, coughing with sputum and difficulty breathing. Ingestion of large doses can cause nausea, headaches and loss of consciousness. Contact with skin and eyes results in irritation and conjunctivitis followed by lens damage and photophobia, respectively. In addition, prolonged exposure to sulfur can result in or worsen pre-existing chronic conditions, and of these, people with skin problems are the most affected [5].

Thus, monitoring in industrial oil processes, natural gas manufacturing, coking coal, wastewater treatment and processing units is important, which can be done based on their physicochemical and biological properties. The presence of H2S in different environments is controlled by different bodies, which set limits ranging from ppm (μg g-1) to ppb (ng g-1) [6]. Several methods have been used for gas measurement, such as chromatography, spectrophotometry and electrochemical techniques. Considering that the detection of H2S can be performed in aqueous solution, since it is in equilibrium with HS- and S-2 sulfides in this type of solution, it is possible to use biomolecules, such as enzymes, to perform the measurement. Therefore, it is possible to modify the surfaces of bio/nanosensors to identify target molecules, such as "X", different from molecules "Y", "B", "A" and "O", whose binding is unlikely. (Fig. 01).

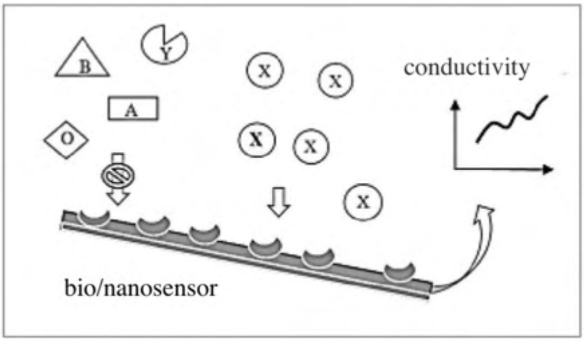

Figure 1: Functional scheme of a Bio/nanosensor.

Source: Authors, 2020.

Comparing to different techniques, detection using electrochemical sensors through biosensors offers great practicality and selectivity, in addition to the possibility of miniaturization, rapid response and low cost. A biosensor is classically defined as a device that incorporates a biological recognition element (enzymes, antibodies, etc.) in intimate contact with a transducer element. [7] (Fig. 02). This integration ensures convenient conversion of biological events into a quantifiable electrical signal.

The role of nanotechnology on the advancement of biosensors and biomimetic sensors has led to an increasing improvement in diagnostic properties, producing Nano-MIPs and nanobiosensors.

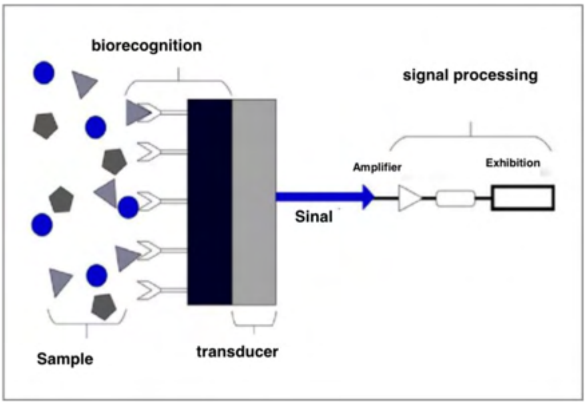

Figure 2: Illustrative scheme of the constitution of a biosensor

Source: Adapted from Hammond (2017).

Among carbon nanomaterials, graphene has received great prominence and, when combined with conductive polymers such as polypyrrole, has guaranteed good analytical responses. This is due to the high electron transfer resulting from the synergism between the materials, since polypyrrole has aromatic rings and high charge storage capacity. [8]. In this sense, since it is intended to achieve low detection limits, the in situ synthesis, with the solution containing the H2S mixture (template molecule), pyrrole monomers (or others with conductive properties, such as thiophene and its derivatives) and the graphene (carbon nanostructures), which will support the sensors.

Dessa forma, essa revisão sistemática tem como principal objetivo a busca de pesquisas experimentais e computacionais de nanosensores baseados em grafeno utilizados para detecção e monitoramento do Sulfeto de Hidrogênio.

METHODOLOGY

This systematic review seeks to investigate the development and use of nanosensors for H2S detection. The articles were obtained using the following search platforms: SienceDirect, PubMed, IEEE Xplore and Scopus. The keyword combinations used within the search engines were “nanosensor AND graphene AND hydrogen sulfide” and “nanosensor AND graphene AND (hydrogen sulfide OR toxic gas) AND (detection OR design)”.

Inclusion criteria encompassed all articles that designed, developed and used bionanosensors to identify H2S. There was no restriction on the year of publication, the language used was English and the type of publication was restricted only to articles published in the journals already described.

Thus, this review was based on the four-step flowchart (PRSMA – flow diagram), whose division is restricted to identification, screening, eligibility and included. This is described in Figure 03 following the criteria of systematic reviews [9].

RESULTS AND DISCUSSION

From the filtering and analysis of the eight (8) selected articles, it was possible to observe that half (4) of the studies carried out for the detection of Hydrogen Sulfide will take place through simulations and computational calculations through software, while the another four (4) articles are experimental studies. Thus, taking into account its toxicity, more analyzes and experimental studies are necessary, in addition to the validation of the prototype in question.

Currently, environmental protection, health and safety issues make gas sensors become essential elements in modern society [10]. The main limitations of this technology include the ability to last and measure the gases, that is, it is necessary to develop a high sensitivity, fast response, low consumption and greater stability [11]. Thus, carbon derivatives, as well as graphene, have been gaining prominence when it comes to easy synthesis, low cost and excellent electrical properties. These advantages are a consequence of its high surface area (/ cm2) and ease of functionalization as it contains carboxylic, epoxy and hydroxyl groups. In recent years, graphene sheets (GS) are considered an applicable material in the production of chemical and biological sensors [12]. Thus, various materials can be used together with graphene to develop more specific and optimized prototypes. Detection performance can be controlled by modifying detection layer properties such as grain size, porosity, thickness, morphology and impurities by altering the surface with new metals [13].

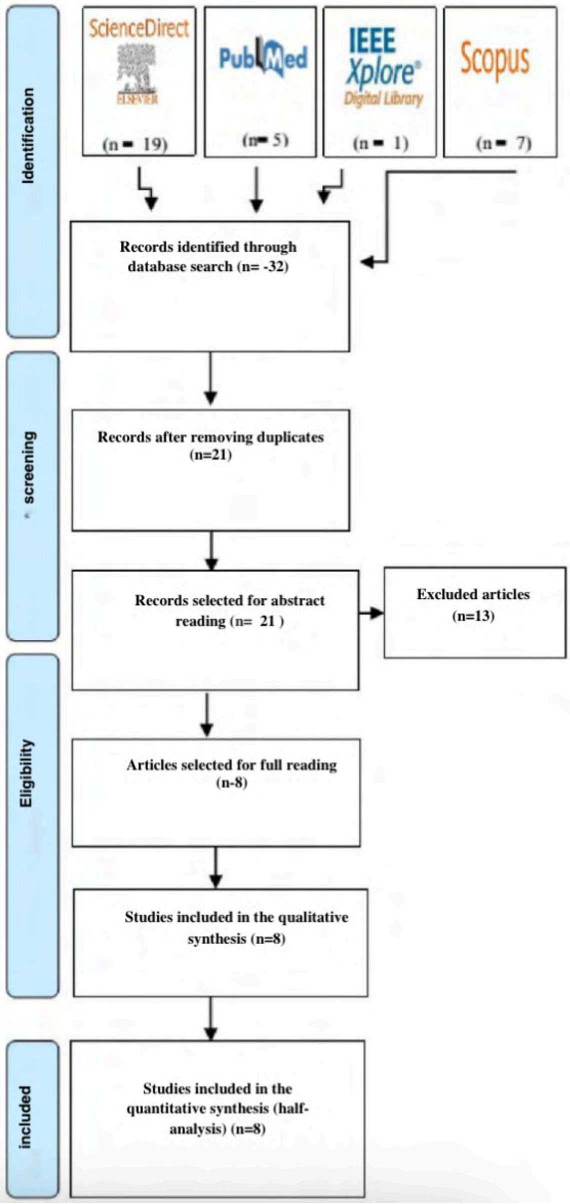

Figure 3: Illustrative scheme of the constitution of a biosensor

Source: Adapted from Hammond (2017).

Metal oxide-based sensors offer the advantages of low cost, power consumption, online detection, and high compatibility with microelectronic processing [4]. However, its disadvantages include low selectivity, stability, long response and recovery time, among others. Thus, to overcome these disadvantages, it is necessary to modify the detection surface with other sensitizing metals and/or metal oxides such as Ag, Au, Fe, Pd, Cu and NiO, CuO, SnO2, Fe3O2, ZnO, Cu2O, WO3, respectively. [4] [14],[15],[16], [17], [18].

According to Lonkar et al., (2016) copper oxide (CuO) is considered a great metallic solvent for removing hydrogen sulfide from various gas streams due to thermal stability as well as thermodynamics in the sulfidization reaction. On the other hand, Mohammadi-Manesh et al., (2015[a]) also state that cuprous oxide (Cu2O) is an excellent semiconductor due to its optical and electrical properties. In addition, it is important to note that copper-based solvents do not suffer volatility problems when compared to other metals. Also in this study, CuO nanoparticles were dispersed on the surface of graphene platelets to detect sulfur molecules at room temperature. This nanostructured hybrid was able to more easily adsorb H2S, ensuring a huge potential for use in monitoring it.

Vuong et al. (2015) describe those sensors based on tungsten oxides (WO_3) have excellent selectivity for both H2S and other toxic gases due to their electrical resistances. In this experiment, the authors developed a WO_3 nanowire structure embedded with porous gold (Au) to detect Hydrogen Sulfide. In addition to great detection performance, these gold-embedded nanowires ensure even greater performance due to the conductive properties of gold.

Asad et al., (2015) describe flexible and selective high-sensitivity H2S sensors based on single-walled carbon nanotube (SWCNT), decorated with Cu nanoparticles. This study shows remarkable responses after exposure to various concentrations of Hydrogen Sulfide, in addition to a rapid response and recovery time. Furthermore, Alaie et al., (2015) developed a selective H_2S sensor using graphene oxide functionalized with dodecylamine and ethylenediamine. These offer great advantages such as remarkable potential for mass production due to their ease of manufacture, selectivity and detection performance. [2]

In turn, Marjani et al., (2020) detected H2S through computer simulations using scandium-doped phosphorene. This study deals with the detection capacity of two phosphorene sensors through the fundamental theory of density (DFT). A similar experiment was developed by Mohammadi-Manesh et al., (2015[a]) handling graphene decorated with Cu and CuO as a nanosensor to detect H2S at room temperature also by means of DFT. Nevertheless, another work also published by Mohammadi-Manesh et al., (2015) describes theoretical studies on electronic structures and electrical conductance at room temperature of Cu2O-GS nanosensors for H_2S detection. Finally, still following the computational experiments, Mohammadi-Manesh & Rahmani, (2017) used a ZnO-GS nanosensor to detect H_2S at room temperature by the same method as the DFT.

Currently, these nanosensors are characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and field emission microscopy (FE-SEM). Raman spectroscopy, thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) and energy dispersed spectroscopy (EDS). While the characterizations and computational optimizations are carried out through periodicals of density functional theory (DFT), extension of the plane wave function, software such as *Quantum Express*, generalized gradient approximation (GGA) with Perdew-Burke-Enzerhof (PBE) function, between others. These computer simulations guarantee a large number of tests, low cost, risk reduction and fast response when compared to the experiments themselves. Experimental research, on the other hand, offers control over variables, better identification of cause and effect, duplication of results, combination with other methodologies and also guarantee the possibility of collecting data at the moment they are happening, without the need for artificial situations.

From the mentioned facts, it is possible to perceive that most of the studies carried out using nanosensors have compounds and derivatives based on copper (Cu) as their main constituent. The combination of graphene and copper guarantees advantages such as high selectivity, sensitivity, electrical conductivity, fast response and low cost. The results obtained from the filtering of the articles are described in Table 01.

FINAL CONSIDERATIONS

Hydrogen Sulfide is one of the most dangerous toxic gases for living organisms and the environment, so it is necessary to develop and apply more efficient alternative methods for its monitoring. From the filtering of the articles, it is noticed that the literature is scarce of studies involving specific nanosensors for the H2S. However, the selected articles presented a great source of information that can be used in future studies.

Among the main materials described here, the most used together with graphene are copper compounds, as well as their derivatives. This combination ensures greater efficiency, as well as optimal responses and recovery from the nanosensors. Both the experiments and the simulations presented prototypes that can and should be used to monitor H2S, especially in environments with risks of contamination and on platforms for extraction and production of oil and gas. Thus, possible contamination risks can be avoided by employing selective, specific, low-cost and rapid detection nanosensors.

Articles	Authors/year	Recognition Elements	Manufacturing process	Description	Rating range	Results
01	Marjane et al., 2020.	Scandium-doped black phosphorene	Computer simulations (DFT)	Perdew-Burke-Eernzerh (PBE) and base set SVP	Adsorption and gas detection to pristine monolayer (BP) and scandium doped (SP) sensors	Electrical sensitivity 16 times greater; more efficient operation and recovery (4.7 ms)
02	Alaie et al., 2015.	Dodecylamine, ethylenediamine and graphene oxide	Interdigitated electrodes (IDT)	X-ray, XPS, FTIR and SEM	Up to 50 ppm	High response at various temperatures and concentrations
03	Mohammadi-Manesh & Rahmani, 2017.	Graphene sheets decorated with zinc oxide (ZnO-GS)	Computer simulations; DFT, flat wave function extension and the QUANTUM ESPRESSO software	GGA with PBE function	Adsorbs with energy of −0.73 V°	Poor adsorption on pure graphene sheets and rich in ZnO-GS nanostructures
04	Lonkar et al., 2016.	Nanostructured graphene hybrid with CuO	*In situ* thermal annealing	XRD, XPS, TEM, SEM, Raman, TGA and N2 physisorption	Adsorption of 1.5mmol H2S/g-sorbent	High adsorption capacity at room temperature
05	Vuong et al., 2015.	WO3 nanowires soaked with Au	WO3 deposition in porous SWCNT model, immersion in HAuCl4 and oxidation	SEM, TEM, XRD, XPS and current voltage measurements	Detection from 10 ppm at different temperatures	Enhanced selectivity with Au
06	Mohammadi-Manesh et al., 2015.	Cu2O-GS Nanosensor	Computer simulations; DFT, flat wave function extension and the QUANTUM ESPRESSO software	GGA with PBE function	Adsorbs in three states; −0.76 V°, −0.78 V° and −0.68 V°	High detection sensitivity
07	Mohammadi-Manesh et al., 2015a.	Graphene decorated with Cu and CuO	Computer simulations; DFT, flat wave function extension and the QUANTUM ESPRESSO software	GGA with PBE function	Adsorbs with energy of −0.88 V° and −1.23 V°	CuO has more sensitivity
08	Asad et al., 2015.	SWCNT-based sensors decorated with Cu nanoparticles	Deposition of Cu nanoparticles in SWCNT model, Interdigitated Electrodes (IDT)	FE-SEM, Hitachi S4160 and EDS	Range from 5 ppm to 150 ppm	Fast response and recovery time

Table 01: Summary of the main information taken from the filtering of the analyzed articles.

Fonte: Autores, 2020.

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