


Review

Graphene-Based Hydrogen Gas Sensors: A Review

Anna Ilnicka ^{1,*}  and Jerzy P. Lukaszewicz ^{1,2}

¹ Faculty of Chemistry, Nicolaus Copernicus University in Torun, Gagarina 7, 87-100 Torun, Poland; jerzy_lukaszewicz@o2.pl

² Centre for Modern Interdisciplinary Technologies, Nicolaus Copernicus University in Torun, Wilenska 4, 87-100 Torun, Poland

* Correspondence: ailnicka@umk.pl; Tel.: +48-609273793

Received: 17 April 2020; Accepted: 22 May 2020; Published: 25 May 2020



Abstract: Graphene is a material gaining attention as a candidate for new application fields such as chemical sensing. In this review, we discuss recent advancements in the field of hydrogen gas sensors based on graphene. Accordingly, the main part of the paper focuses on hydrogen gas sensors and examines the influence of different manufacturing scenarios on the applicability of graphene and its derivatives as key components of sensing layers. An overview of pristine graphene customization methods is presented such as heteroatom doping, insertion of metal/metal oxide nanosized domains, as well as creation of graphene-polymer blends. Volumetric structuring of graphene sheets (single layered and stacked forms) is also considered as an important modifier of its effective use. Finally, a discussion of the possible advantages and weaknesses of graphene as sensing material for hydrogen detection is provided.

Keywords: gas sensor; hydrogen sensor; graphene; graphene oxide; reduced graphene oxide; functionalized graphene; semiconductor; metal oxide; metal; polymer

1. Introduction

Contemporary life and technology are overwhelmed by the trend of automation that is based on informative data acquisition and processing to trigger appropriate decisions and corresponding actions. There is a variety of chemical and biological species which must be monitored with concern for safety, health, environmental concerns, and specific technical issues. The scope of species to be detected ranks from DNA to atmospheric pollutants like NO_x [1]. International Union of Pure and Applied Chemistry (IUPAC) denoted a sensing material as a key element of chemical and biological sensors [2]. In the classic understanding of the term, a biological sensor (biosensor) is a bio-originated material/substance which plays the role of a sensing material. A chemical sensor, on the other hand, does not rely on bio-originated sensing materials. It is impossible to review all sensing systems, i.e., substance to be detected–sensing material–sensing principle, in a short paper. Such efforts would require a multivolume encyclopedia. Thus, a single review article in the area of sensing must and can only be focused on a specific target, one that is well justified by its applicability to real life. The second motivation should be the novelty of the sensing system’s basic elements, which might uncover new technical features and application possibilities. The major aim of the current paper is to present the latest trends and achievements in the sensing system defined by hydrogen as the chemical substance to be detected and graphene-based materials as the sensing materials.

Hydrogen is often called the energetic medium of the future. The following sentences, spoken at the World Economy Forum, perfectly summarize the merit of hydrogen perspectives: “Hydrogen is a rising star. Versatile and environmentally friendly, hydrogen produces no CO₂ when combusted, only water and heat. It can be used to decarbonise electricity, heating, transport, and industry. A clean

energy vector, hydrogen is easily transported, stored, and blended with current fuels” [3,4]. Aside from these breakthrough horizons, however, there is another side to hydrogen stemming from its chemical nature. Hydrogen is a dangerous gas and easily escapes through leakages and even penetrates some solids. When mixed with air, it creates an explosive mixture characterized by a high explosion energy in a broad range of proportions: the Lower Explosive Level (LEL) equals 4% vol. and the Upper Explosive Level (UEL) equals 75% vol. Hydrogen is odorless, tasteless, and tintless and therefore hydrogen is “invisible” to human and animal senses and implementing artificial sensing devices/sensors is indispensable. It is certain that the scale of hydrogen use will increase and scatter along with the growth of a global hydrogen economy. Beside the known industrial consumers of hydrogen and known processes (among others, ammonia synthesis, petroleum product conversion, methanol synthesis, reductive metallurgy, etc.), a new sector of individual hydrogen users will appear soon and grow rapidly [5]. This applies first to hydrogen-powered vehicles and hydrogen storage/tanking stations. All these technical facilities will need to be equipped with hydrogen sensors to avoid its uncontrolled release and expected consequent explosions. In this sense, hydrogen may be seen as more difficult to handle than other potentially explosive gases, like Liquefied Petroleum Gas (LPG) and Compressed Natural Gas (CNG).

Carbon is an exceptional element offering a broad range of unique properties depending on its structure and chemical composition. The list of carbon-based material applications ranges from construction materials (carbon fiber composites), through electric conductors (graphite), up to precious jewelry items (diamond) [6,7]. It is impossible to find any other element which could offer a similarly wide range of structures, compositions, properties, and applications. It is no wonder that carbon, in its diversified forms, attracted the interest of the chemical sensing scientist society quite quickly. First research announcements are dated to the beginning of the 1980s. To the best of our knowledge, the papers by Lukaszewicz were the first summaries to describe the application of semiconductor carbon films specifically as resistive humidity sensors [8,9]. Since the early years of the twenty-first century, the number of papers describing the applicability of carbon-based materials has been continuously increasing. The presented approaches cover nearly all known forms of carbon.

The variety of physico-chemical properties of carbon-based materials, including graphene, is a key feature that makes these materials more attractive for sensing than others, like semiconducting transition metal oxides. The fundamental property of a sensing material is the capability to interact with the species to be detected and alter in this way the original properties of the sensing material. The most obvious and common interaction is the adsorption of analyte atoms/molecules onto the surface of the sensing material. Thus, any processing of graphene, and other carbon-based materials as well, which aims to increase its adsorption ability is of high interest. Generally, two main processing categories should always be considered: the creation of heterogenous adsorption centers and/or tailoring the material’s structural parameters, e.g., the specific surface area and pore structure (including pore size distribution).

1.1. Surface Functionalization of Graphene and Other Carbon Materials by Creation of Surface Heterogenous Centers

Carbon materials, including graphene, with the partial exception of diamond, are susceptible to heteroatom insertion due to chemical reactions in its gas and liquid phase. The most common, which in fact may proceed spontaneously in air for certain types of carbons, is oxidation consisting of creating of so-called oxygen surface functional groups: hydroxyl, carbonyl, lactone, and carboxyl. Surface oxidation can be accelerated (or exclusively triggered in the case of graphene) by means of strong oxidants such as gaseous oxygen at an elevated temperature, air, H_2O_2 , KMnO_4 , and HNO_3 (chemical oxidation) [10]. The intensity of spontaneous and strong-oxidant-forced oxidation depends, among others, on the type of carbon material subjected to the process. Carbon black, pyrolytic chars, and activated carbon are susceptible to spontaneous oxidation even while chemical oxidation leads to intensive oxygen insertion. Conversely, so-called nano-carbons, like carbon nanotubes and graphene,

are hardly oxidable by atmospheric oxygen at room temperature and severe chemical oxidation conditions must be implemented to ensure effective oxidation. Similar rules are applicable to graphite, which can be treated pieces of multilayered graphene. Surface oxygen functional groups make such modified surfaces more hydrophilic and generally, once oxidized, the surface is more capable of attracting polar species. Intensive oxidation may have a positive impact on the structural parameters, too. Oxidation may create voids, i.e., pores, in the carbon matrix. Other elements, e.g., nitrogen, are able to insert themselves into the carbon surface analogously to oxygen, though spontaneous nitrogen insertion in contact with air is not possible. Similarly to oxygen functional groups, the nature of nitrogen surface species has been investigated intensively and is well known [11]. Nitrogen insertion into carbon matrixes (especially activated carbons, graphite, and graphene) has been under review recently due to its theoretical and practical applicability as electrode material in electrochemical energy generators and storage devices. Insertion of other elements is rarely reported, as is their applicability.

In the case of oxygen and nitrogen surface species, these elements are chemically bonded to the carbon matrix and even to six-membered condensed rings (graphene-looking structures) [12]. This ability is often limited in the case of metals and their derivatives, particularly oxides, when they are deposited onto carbon surfaces. Transition metals/metal oxides are of special interest in chemical sensing due to their expected and confirmed adsorption affinity to many detectable reducible species, like hydrogen, carbon monoxide, nitrous oxide, nitric oxide, and ammonia. Additionally, metal/metal oxide domains, even when deposited on carbon surfaces, preserve the ability of catalytical conversion of the detected species, which usually triggers side effects such as the release of heat, capture/release of electric current carriers, shift of the Fermi Level in the surface region, and/or production of secondary chemical substances during a catalytic process. These side effects could be of additional merit in the entire sensing mechanism. It must be stated that the carbon matrix, like graphene sheets and with the exception of diamond, has evident reductive properties which become clearly visible in contact with transition metal ions in a water solution. Some of these cations are reduced to a metallic form spontaneously, forming nano-sized metal domains on the carbon surface [13]. This especially applies to easily reducible metals like gold, silver, and copper. For example, simply dipping certain carbon materials (including graphite) in a water solution of silver ions results in the creation of metallic silver nano-domains upon contact with the carbon surface and its reductive influence. In the case of other transition metal cations, like iron, manganese, zinc, etc., the spontaneous reduction to metallic clusters in a water solution does not occur. Every carbon-based material that has been impregnated this way is then dried and elaborated at an elevated temperature in an inert atmosphere (protection of carbon matrix against burning); this results in the conversion of metal ions into metal oxide nano-domains/clusters [14,15]. These clusters may exhibit catalytic activity towards the species under detection. As mentioned previously, the catalysis is often a source of secondary effects which can be exploited in the basic sensing process.

1.2. Carbon Surface Functionalization by Tailoring Structural Parameters

Adsorption of chemical species to be detected onto the surface of sensing materials proceeds owing to strong specific (chemical adsorption) interactions and weak, non-specific (physical adsorption) ones. Commonly, physical adsorption is considered to also be the first, unavoidable step in chemical adsorption. Thus, physical adsorption on solids is a spontaneous process that always occurs at the gas-solid interface, i.e., in the system: detected substance–sensing material. Adsorption potential in pores is always higher than on a flat surface, even when the chemical nature of the adsorbing material is the same. The curvature of the surface in pores leads the forces of neighboring walls to overlap, provided the pores are narrow enough (micro- and meso-pores, classed according to IUPAC classification). Improved pore structure is the main consideration when evaluating the surface area of any material. A larger surface area enables the higher physical adsorption of the species that is to be detected, not just for geometric reasons, but also due to the increased number of surface functional groups/clusters that usually exist on a solid's enhanced surface. Therefore, any carbon

material processing that leads to the improvement of carbon matrixes' pore structure may be of interest in relation to its sensing application.

Recently, several studies were performed on the 3D structuring of graphene flakes into volumetric porous structures built of graphene sheets of different agglomeration degrees. When occurring in the form of nanosized flakes, in most cases graphene undergoes spontaneous self-stacking due to dispersive attraction forces often called π - π stacking [16]. The existence of these forces results in the formation of graphene agglomerates. Thus, beside single layered graphene (SLG), other agglomerates also exist, such as few layered graphene (FLG) and multilayered graphene (MLG) [17,18]. Graphite may be considered a terminal state of the self-stacking process. The stacking process is an effective one, seeing as secondary splitting of graphene agglomerates requires complex methods, like mechanical adhesive type exfoliation, liquid phase organic solvent exfoliation assisted by sonication and/or microwaves, electroexfoliation, oxidation to graphene oxide followed by chemical bonding of the flakes, etc. [19]. Nevertheless, exfoliated graphene flakes may efficiently bond with a porous solid applicable to chemical/hydrogen sensing.

2. Hydrogen Gas Sensors

The analysis of Web of Science data prove that a continuous growth in hydrogen sensor SCI publications in the last 10 years, reaching ~640 in 2019 (Figure 1). This report strongly indicates that investigating of hydrogen sensors is one of major trends in the field of gas sensors.

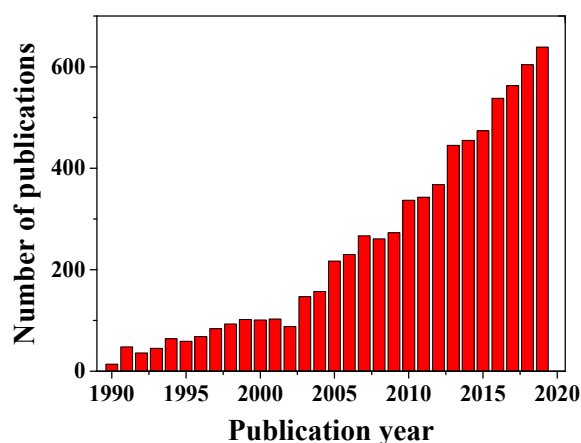


Figure 1. The increasing number of papers in the field of hydrogen gas sensors from 2001 to 2020 (internet search on the Web of Science, 15 March 2020). Keywords for search: hydrogen gas sensor.

2.1. Semiconductor Metal Oxides as Receptor Materials for Hydrogen Sensing

The investigation of different hydrogen receptor materials is motivated by the importance of sensing this gas in particular. The first historical semiconductor sensor for reductive gases was the Taguchi SnO₂ sensor invented in 1968 and later patented [20]. Taguchi employed a nano-structured and defected SnO₂, in fact a n-type semiconductor. Originally, the sensor was designed to detect liquid petroleum gas (LPG) and solve a serious problem of LPG explosions in Japan. The sensing mechanism involves the catalytic oxidation of reductive species, like LPG, but other reductive gases, such as hydrogen, may interact with the sensing material in the same manner. The exclusive presence of oxygen combined with the lack of reductive gaseous species (LPG, hydrogen etc.), oxygen molecules get adsorbed onto the SnO₂ surface, which causes an intensive depletion of electrons on this surface [21]. Thus, the boundary potential barriers in the polycrystalline SnO₂ increase dramatically, restricting electric current conduction through the receptor layer. When gaseous reductive species encounter a SnO₂ surface depleted this way, electrons bonded to the chemisorbed O₂ molecules get released, which triggers a spectacular increase of electric conductivity of the sensing material. This sensing idea spread quickly in the field of LPG sensing, and for hydrogen as well [22]. Over the past decades, the general

principle of n-type SnO_2 semiconductor sensors for hydrogen and other gases was broadened to other metal oxides, like SnO , ZnO , V_2O_3 , Fe_2O_3 , Mn_2O_3 , Co_3O_4 , Cr_2O_3 , TiO_2 , WO_3 , NiO , In_2O_3 , CuO , SrO , Nb_2O_5 , GeO_2 , MoO_3 , La_2O_3 , Ta_2O_5 , Nd_2O_3 , CeO_2 , and this research direction is very active to this day [23–31]. The relatively high operating temperature of even up to 300–400 °C was a key negative feature of early SnO_2 -based hydrogen sensors. This problem was solved by the addition of metal nanoparticles to SnO_2 and other semiconductor oxides [32–36]. Typically, Au, Ag, Pt, Pd, and Sb were used for semiconductor metal oxide doping. This methodology managed the operational temperature problem and allowed tailoring the detection level and selectivity of the sensing material. Even today the semiconductor metal oxide sensing principle is widely exploited in commercial hydrogen (and other reductive gases) detecting devices, for example that produced by Figaro Inc. co-founded by N. Taguchi, the inventor of the SnO_2 gas sensor [37].

2.2. Other Sensing Materials Applicable to Hydrogen Sensing

The heart of a hydrogen sensor described above is the nanostructured (nanograins, nanowires, nanofilms, etc.) sensing semiconductor metal oxide interacting with a reductive gas under detection (including hydrogen). Thus, researches have concluded quite early that the semiconductor metal oxides may be replaced by other semiconductors of inorganic or organic character. This research trend primarily includes inorganic metal sulfides like MoS_2 , CdS , TiS_2 , and SnS_2 [38–40]. Similarly, in metal sulfides used as the basic sensing material, the addition of metal nanoparticles lead to enhanced operational parameters, such as operating temperature, sensitivity range, durability, and selectivity. Thus, the examination of metal sulfides mirrors, in a way, the original experiment with semiconductor metal oxides.

Metal oxides and sulfides are not the only materials exhibiting adsorption properties towards various gases in parallel with semiconductor properties. This means that other classes of semiconductor materials were and are of interest for hydrogen sensing. Semiconductor polymers and nanocarbons can be thought of as two materials engineering emerging research fields. Quite naturally, researchers' attention has recently come to focus on these polymers and carbons. The geometrical form of these sensing materials is broad and the structures that can be fabricated and investigated include carbon/polymer wires, dots, films, tubes, sheets, powders, etc.

Polyaniline and polypyrrole are commonly modified by the insertion of metal nanoparticles [41–45]. In general, the same concept of creating sensing materials is largely repeated, i.e., a semiconductor background decorated with metal domains is explored the most in papers on hydrogen sensing by means of conductive polymers.

The same idea of how hydrogen sensing material can be made spread onto nanostructured carbon-like carbon nanotubes and dots after their discovery. The applicability of carbon nanotubes for chemical sensing of reductive species, including hydrogen detection, has been reported on as well [46]. A more general review of the applicability of carbon forms/materials (porous carbons, carbon nanotubes, graphene) for gas sensing was presented recently [47]; however, no emphasis was placed on hydrogen detection in particular. An overview of the problem of hydrogen sensing has not long ago been reported by Chauhan and Bhattacharya [48]. However, even with this much research and review, there is still a need to summarize the applicability of graphene and its derivatives for hydrogen sensing, paying special attention to the semiconductor principle of operation; this is the main target of this work [49–57]. Graphene and its derivatives present diversified useful properties, such as susceptibility to the insertion of surface functional groups and metal clusters, steerable electric properties and morphology. All these facts make graphene and its derivatives attractive candidates for hydrogen sensing based on the chemoresistor principle.

2.3. Graphene-Based Materials for Hydrogen Sensors

Graphene is a material which theoretically should behave similarly to CNTs. In general, the advantage of graphene over CNT is the lower price of graphene, but its derivatives may also be

produced more inexpensively than other graphitic carbon materials, e.g., carbon nanotubes. Hence, the current decade has seen graphene attract the close attention of gas sensor researchers. Better chemical affinity and selectivity of graphene over other carbon materials can be achieved by the functionalization of graphene or reduced graphene oxide [57,58]. Another advantage of sensors based on graphene, in contrast with other solid-state gas sensors, is operation temperature. In certain design conditions a graphene sensor may be room temperature operable. Thus, a low energy consumption may attribute to such hydrogen sensors [59–62]. Furthermore, the graphene films owe to their flexibility let to construct hydrogen sensing devices subjected to intensive bending forces [60]. The nanocomposites that contain graphene and noble metals improve hydrogen gas sensing properties. These properties include higher and faster response, cross sensitivity, quick recovery, long term stability, and repeatability of the sensor [63,64]. Graphene has a minute concentration of unsaturated valences which would provide the chemisorption of hydrogen molecules on its surface. Consequently, many researchers use doping or surface modification to resolve this problem, especially using catalytic noble metal ions [65,66]. The use of graphene in gas sensors requires different modifications with metal, polymers, or other appropriate modifiers of other kind. The next three sub-sections contain descriptions of the possible functionalization of graphene to improve its properties to detect hydrogen.

2.3.1. Graphene-Polymer Modified

Some studies prove that the multicomponent composites like metal-carbon-polymer materials are might be useful for the detection of H_2 . The functional groups bonded to graphene planes interact intensively with polymer domains of high polarity. These interactions are helpful to make such durable composites. Additionally, a synergic effect regarding sensing properties is expected resulting from complementarity of the electric and chemical properties of the components. The addition of metallic nanoparticles is a typical sensitization measure that upgrades H_2 gas adsorption due to catalytic dissociation of H_2 molecules. Such created H atoms easily diffuse into the interstitial sites of some metals.

One of the proposed modifications of graphene is functionalizing with polymers. Conducting polymers and their nano-derivatives are a good candidate for the role of sensing layers and have been under investigation because of their excellent reliability. Such materials are valuable due to high sensitivities and cost effectiveness. The porous poly (3,4-ethylenedioxythiophene) (PEDOT) nanostructure has been durably deposited on the surface of reduced graphene oxide (RGO) layers by means of a fast thermal processing during the in-situ polymerization of a 3,4-ethylenedioxythiophene (EDOT) monomer [67]. Zheng et al., describe graphene/(3,4-ethylenedioxythiophene)-PEDOT:poly(styrenesulfonate)-PSS nanocomposite films for the construction of hydrogen sensors. The key sensing parameters, i.e., sensitivity, response, and recovery time of the composite toward the chemical signal of 100 parts per million (ppm) H_2 were: 4.2% and ~30 s. Response time for rGO/PEDOT:PSS and PEDOT:PSS was, respectively, five and seven times longer than for GO/PEDOT:PSS [68].

A paper by Al-Mashat et al. reports manufacturing of a graphene/polyaniline (PANI) composite subsequently utilized as a hydrogen sensor. The noticed sensitivity was 16.57% toward the chemical signal of 1% of H_2 . The sensitivity was considerably better than the sensitivities of analogous hydrogen sensors but made separately of graphene sheets (0.83%) or PANI nanofibers (9.38%) [69]. Zou et al., describe in their work a composite of PANI and reduced graphene oxide doped with palladium nanoparticles for the purpose of room temperature hydrogen-gas sensing [70]. Figure 2a presents the sensing characteristic of a Pd-PANI-GO film to different concentrations of hydrogen. The analyzed sensor was reacting fast and provided a noticeable response to high concentration of hydrogen. The linear relationship was found for growing concentration of hydrogen in the range from 0.01 to 2 vol% (Figure 2b). Figure 3a presents gas response for 1% of hydrogen using the rGO, PANI, PANI-GO, and Pd-PANI-GO as sensors. Additionally, the cross sensitivity to CH_3OH , CO_2 , and H_2S for Pd-PANI-GO sensor was examined (Figure 3b). The sensor was insensitive to CO_2 and H_2S , while it reacted to the presence 1 vol% CH_3OH (electric conductivity increased by <8%). The selective

adsorption affinity of Pd nanodomains towards hydrogen was claimed to be the key reasoning behind the selectivity improvement.

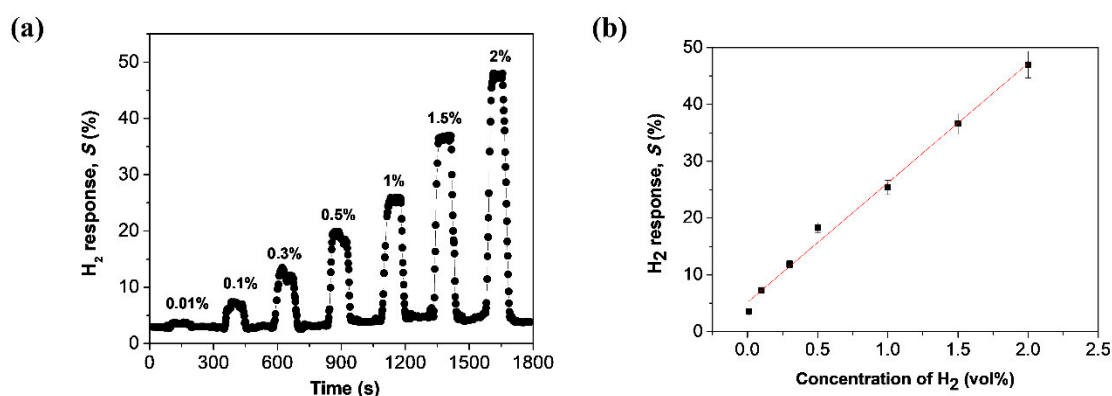


Figure 2. (a) Gas-sensing response of the P-PANI-GO-based sensor to different concentrations of hydrogen at room temperature; (b) The linear response for gas concentration in the range from 0.01 to 2 vol% [70]. Copyright (2020), with permission from Elsevier.

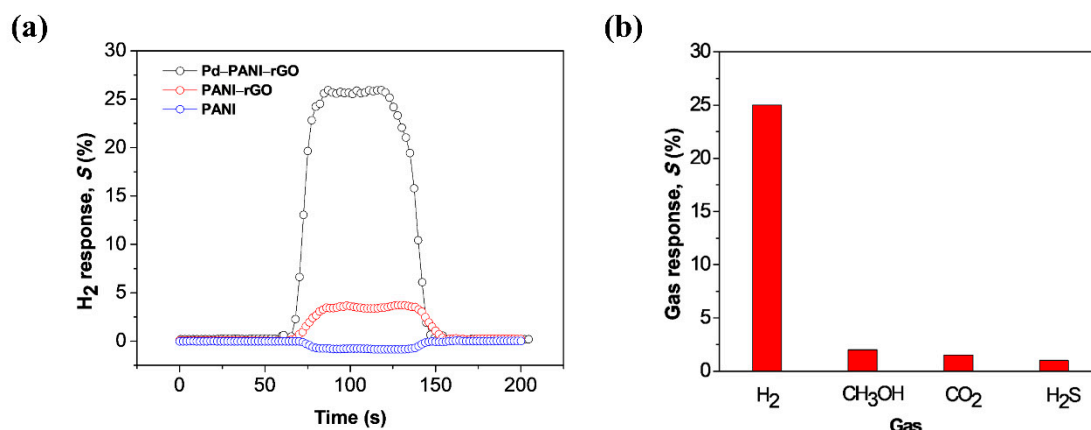


Figure 3. (a) Responses of the rGO, PANI, PANI-GO, and Pd-PANI-GO for hydrogen sensing (1%) at room temperature; (b) Response of the Pd-PANI-GO-nanocomposite-based sensor to various gases [70]. Copyright (2020), with permission from Elsevier.

Apart from the conducting polymer PANI, poly (methyl methacrylate) (PMMA) has also been applied as separation medium restricting the access of undesired chemical species to a hydrogen sensor. One such study is announced by Hong et al., who utilized PMMA as a selective membrane protecting Pd-coated single-layer graphene against the contact with interfering molecules. In this approach the single layered graphene was deposited by means of the chemical vapor deposition (CVD) on a Cu substrate. After etching of the Cu background, graphene was Pd coated by a galvanic transfer reaction using PdCl₂. The bi-layered material was finally spin coated with a thin membrane of PMMA. The channels being present in the PMMA membrane coating allow H₂ molecules to penetrate through; this is because of H₂ has a lower kinetic diameter compared to other interfering molecules: CO, NO₂, and CH₄. In addition, these studies delivered reliable and reproducible sensing properties upon the exposure to a broad range of H₂ concentrations: from 0.025 to 2%. Some other composites were examined to like the PMMA/palladium (Pd) nanoparticle (NP)/single-layer graphene (SLG) hybrid. In this case, the hydrogen sensing performance was spectacularly better than for the graphene-Pd NP hybrid sensors [71]. The sensing parameters of several hydrogen gas sensors incorporating graphene, graphene derivatives, and various polymers are summarized and listed in Table 1.

Table 1. Comparison of the H₂ sensors based on graphene and their composites with polymers.

Sensor Material	Detection Level/Range	Operating Temperature	Response Time	Recovery Time	Ref.
RGO-PEDOT:PSS	100 ppm	RT	~30 s	~25 s	[68]
GR-PANI	1 vol%	RT	~25 s	—	[69]
RGO-PANI	1 vol%	RT	20 s	50 s	[70]
PMMA/Pd NP/SLG	0.025–2 vol%	RT	1.81 min	5.52 min	[71]

where: RGO—reduced graphene oxide; GF—graphene; PEDOT—poly(3,4-ethylenedioxythiophene); PEDOT:PSS—graphene/(3,4-ethylenedioxythiophene):poly(styrenesulfonate); PANI—polyaniline; ppm — parts per million; RT—room temperature.

2.3.2. Graphene-Metal Modified

Graphene is widely described as a base material in hydrogen sensors due to a possible improvement of its surface area and susceptibility of its electronic properties to the changes caused by adsorbing atoms and molecules including hydrogen. However, the pristine graphene sensitiveness to hydrogen is limited. Hence, most of the heretofore reported hydrogen sensors incorporating graphene and working on the resistor principle contain graphene sheets functionalized mostly with Pd or Pt the form of fine particles and/or thin films. These metals are well-known to adsorb selectively with H₂ molecules and are capable to catalyze their split to H atoms [72–74]. Various graphene–nanoparticle hybrid systems, such as graphene modified with transition metals, have been studied in different aspects of gas sensing with the aim to improve the properties of hydrogen sensors. Chu et al. [73] and Shafiei et al. [75] investigated the catalytic effect of Pt nanoparticles on the H₂ sensing properties of such modified layered graphene laid on a SiC. In another paper, Pt/graphene sheets structures were manufactured by reducing spray deposited layer of graphite oxide by means of hydrazine vapor. Current-voltage characteristics and kinetic responses of towards 0.25, 0.5, and 1.0% hydrogen were examined at 100 °C. The sensors were set at a constant reverse bias, as the sensing characteristics was more favorable for reverse bias instead of forward bias. A voltage shift of 100 mV was recorded at a 1 mA reverse bias current [76]. In a similar study, Chu et al. exploited epitaxial CVD deposition of graphene on SiC. The background was previously coated with a Pt layer, playing the dopant role, which phenomenon increased the electric conductance of graphene. Sensitivity test proved that exposure to H₂ diminished the electric resistance of Pt/graphene system. The phenomenon was temperature dependent [77].

After dissociation, atomic hydrogen concentrates on the Pt surface. Then, the hydrogen atoms migrate to the graphene/Pt interface. Hydrogen atoms get bonded covalently to graphene and such a hydrogenated graphene exhibits an increased work function. When the distance between graphene and Pt decreases, it can also lift the Fermi-level towards the conduction band. Consequently, the free carrier concentration increases, raising the electric conductance of the hybrid/Pt device. Sensing performance of hydrogen sensors incorporating Pt-decorated graphene sheets and Pt-decorated multiwalled CNTs was investigated by Kaniyoor et al. The decoration process was performed by means of a drop casting method. Pt/graphene exhibited a similar response times but had twice the sensitivity of Pt/CNT [78]. Pt-loaded (nanoparticles) graphene aerogels manufactured by Harley-Trochimczyk et al. and utilized as a catalytic hydrogen sensor. Several positive sensing features were noticed in this case as: 1.6% sensitivity at 10,000 ppm of H₂, and a short response (0.97 s) and recovery time (0.72 s). Additionally, the sensor operation required a low power (2.2 mW) which parameter is an important shortcoming of catalytic sensors. The detection limit of 65 ppm was considerably low. Cross-sensitivity to other gases was neglectable [79].

Wong et al. announced a H₂ sensor based on Pt-decorated graphene oxide nanostructures. By applying some optimized manufacturing and operational parameters, the sensing device was characterized by 10% sensitivity to the chemical signal of 200 ppm hydrogen (operable at room conditions) [56]. Similarly, a sensor containing a layer of reduced graphene oxide decorated with Pt nanoparticles was fabricated by means of a freeze-drying method and subsequently elaborated by heat treatment. The Pt@rGO nanocomposites prepared this way showed outstanding H₂ sensing

properties at a relatively low operational temperature of 50 °C. A sensor fabricated using the Pt@rGO sensing material is presented in Figure 4a. The responses of Pt@rGO-based sensor were investigated at different temperatures 30–70 °C (Figure 4b). An increase in the operating temperature to 50 °C intensified the sensor response to the presence of hydrogen. The sensitivity toward 0.5% hydrogen was 8%. The response and recovery times of the sensor exposed to 0.5% hydrogen were 63 and 104 s, respectively. Figure 5 depicts the gas-sensing mechanism of a Pt@rGO-based sensor [80].

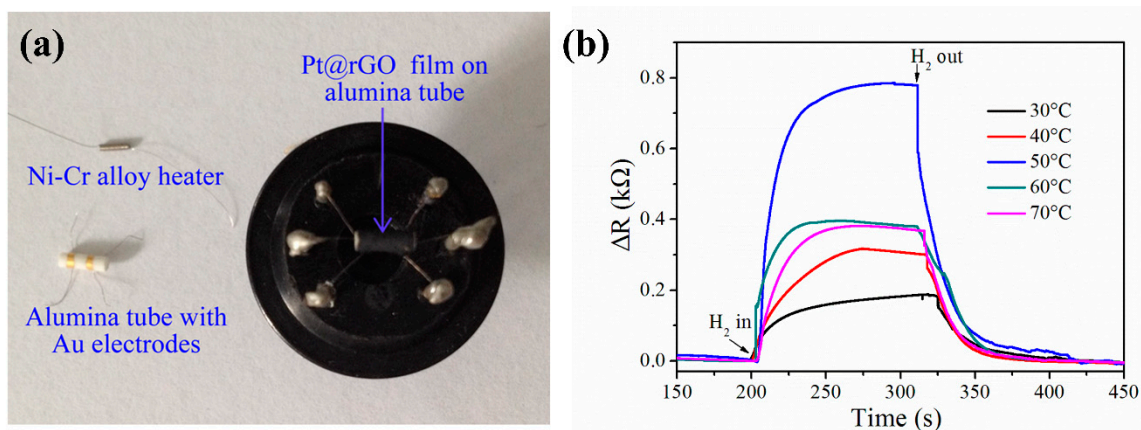


Figure 4. (a) Photography of the sensor; (b) Resistance response of a Pt@rGO-based hydrogen sensor exposed to 3% H₂ in the temperature range 30–70 °C [80]. Copyright (2020), with permission from Elsevier.

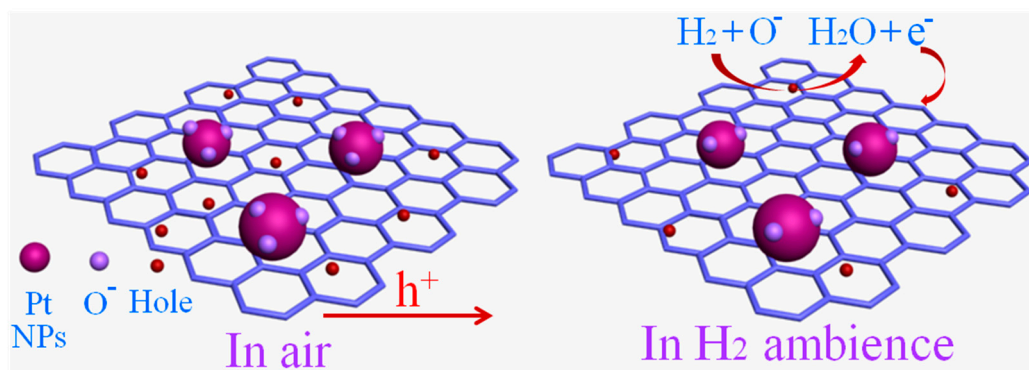


Figure 5. Sensing mechanism of the Pt@rGO nanocomposite sensor toward hydrogen [80]. Copyright (2020), with permission from Elsevier.

In a paper by Zhu et al. Pt-functionalized graphene originated sensor, upon exposition to 100–10,000 ppm of H₂ (20–40 °C range), demonstrated increased resistance performance vs. H₂ concentrations. Conversely, it showed a decrease in resistance when interacting with 10000 ppm of H₂ at 65 °C, or with 500 ppm of H₂ at 105 °C [81]. In another case, described by Yu et al., a Pt/graphene/GaN sensor was constructed and its electrical properties and H₂ sensing characteristics were determined. The study confirmed that graphene is applicable as a hydrogen sensing material and exhibited a sensitivity of 0.9 V toward 1% hydrogen gas in a forward bias at 160 °C [82].

Graphene's work function is considered to be lower than Pd. The work function relationship allows the electron transfer from graphene to Pd. In the presence of H₂, a metal hydride (PdH_x) forms which has a lower work function. Hence, the addition of graphene plays a key role in improving the gas sensing performance of the hybrid sensing material. Pak et al. have manufactured a palladium nanoparticle functionalized GNR array for H₂ sensing. A 90% response time was 60 s at 1000 ppm and fast 80% recovery was achieved within 90 s. The sensor consisting of periodically aligned GNR array with no polymer residue. A chromium interlayer was placed under the polymer residue via laser interference lithography aiming at protecting the graphene surface against strains or doping. Such GNR

sensors had a square response and recovery curve. However, a sensing response of Pd-GNR-based sensors was noticed mainly due to the limited adsorption of H_2 molecules at the relatively small number of Pd-NPs laid on narrow GNRs. Nevertheless, these sensors responded quickly to the increase and decrease of hydrogen gas concentration. The effect was associated to the ease of adsorption and desorption of hydrogen gas molecules on Pd-NPs [83].

In another attempt, Lange et al. investigate a multilayer graphene-palladium nanocomposite supplemented with an Au electrode for hydrogen gas sensing [84]. The Pd-modified graphene was found to be sensitive to H_2 in the concentration range 0.5–1% in synthetic air. Pristine graphene's sensitivity to H_2 is exceptionally low, but incorporating Pd improves the sensitivity spectacularly (by more than an order of magnitude). Sensitivity of the nanocomposite depends on the number of graphene layers in the hybrid structure. Likewise, Johnson et al. describes hydrogen sensing using Pd-functionalized multilayer graphene nanoribbon networks [85].

Hydrogen gas sensors of visible flexibility and operating at room temperature, designed by means of a single layer graphene also modified with Pd nanodomains are reported by Chung et al. [86]. After optimizing, such a graphene-based sensor, with 3 nm thick Pd layer, provides a sensing response of 33% upon the exposure to 1000 ppm H_2 at room temperature. Moreover, this sensor operates well even when it is bent to a curved shape which radius may be as small as 3 mm. The manufacturing technology may be transferred to a broad range of sensing devices demanding mechanical durability, and high gas response. The density of deposited Pd nanoparticles is crucial for sensing characteristics. A similar flexible sensor for H_2 detection is reported by Lee et al., where Pt-rGO was deposited on a radio-frequency identification tag [87]. Aiming at the elaboration of a batch production process of graphene-based hydrogen sensors, a wafer-scale manufacturing scenario was reported as well. Firstly, graphene as a thin film was laid onto a Si wafer. On each wafer, a single gas sensor's dimensions were 4 mm \times 3 mm with. Then, a 1 nm thick palladium film was laid on top of a graphene layer [88]. Similarly, Pandey et al. presents Pd-doped reduced graphene oxide films, usable for detecting 50 ppm of H_2 at both room temperature (35 °C) and elevated temperatures (75 °C) with reproducible sensing characteristics. On Figure 6, there is present a resistance response of Pd-rGO device to 3300 ppm hydrogen at a different temperature and sensor response as a function of temperature [89]. In one of the proposed techniques, Tang et al. show a chemical method to obtain Pd nanoparticles using Pd (bipyridine)(pyrene)₂. In a 10 min immersing time, Pd domains grew on graphene by π - π bonds without causing unwanted defects in the graphene lattice; a subsequent thermal treatment led to formation of Pd nanoparticles. The graphene decorated by Pd nanoparticles let to fabricate H_2 sensors at a wafer scale with high throughput. The sensor's response for 1% H_2 was of 5.88% at room conditions under purple light illumination. The illumination significantly improved base sensing features such as response time (shortening), and particularly the recovery time (considerable shortened) [90].

Phan et al. prepared a Pd-graphene (Pd-Gr) composite, in which Pd spherical nanoparticles were deposited by means of graphene oxide (GO) and Pd precursor in solution. The composite was then applied as H_2 sensor working on a chemoresistor principle. The Pd-Gr composite was capable to detect H_2 at a low temperature [91]. In a later paper of Phan et al., a novel Pd nanocube-graphene hybrid materials for H_2 detection was synthesized and investigated. The Pd nanocubes were synthesized by a chemical method via seed-mediated growth in two steps. In comparison to previously investigated materials like Pd NPs-Gr, Pd cube-Gr hybrids have improved sensitivity (a two-fold increase). The response to the signal of 1000 ppm H_2 was 13% at room temperature, 10.4% at 50 °C, and 9.2% at 100 °C. Moreover, such Pd cube-Gr hybrid sensors had a linear H_2 sensing characteristics in the range from 6 to 1000 ppm (mainly at temperatures of 50 °C). 50 °C seems to be the optimal temperature regarding sensitivity, response time, and repeatability. From what experiments have shown, the Pd cube-Gr hybrid H_2 sensor is operable at low H_2 concentrations, even at a low temperature. The study may be considered an initial step in applying other Pd crystal shapes for manufacturing H_2 sensitive graphene-based composites [92]. Among other concessions, Phan et al. investigates bimetallic metals, such as Ni-Pd, which should prevent H_2 molecules from a deep penetration into the Pd lattice.

This measure should improve the structural stability of such sensing materials. The Ni/Pd-Gr bimetallic composite samples nearly showed a complete recovery and rapid response when returned to the recovery state. At the optimal Ni in Pd percentage of 7% was found. Such bimetal-based H₂ sensor exhibited a linear response from 1 to 1000 ppm, with insignificant hysteresis. The response values found with 1000 ppm H₂ at room temperature were 11 and 9% for Ni/Pd ~7% and pure Pd-Gr, respectively. From this experiment, we know that the low-temperature H₂ sensor based on the Pd-Gr composite can be perfected, in terms of high sensitivity, rapid response, and minimum hysteresis effects, by adding a small amount of Ni to the Pd lattice [93]. Similarly, bimetal modification of graphene decorated by Pd-Ag alloy nanoparticles for H₂ detection is examined by Sharma et al. [64,94]. The maximum gas response was 16.2% at 1000 ppm of H₂. A higher response is noted in a paper by Huang et al. where the graphene sensor exhibited a high hydrogen response, up to 32.5%, when exposed to 1000 ppm hydrogen [95]. Zhang et al. demonstrate an effectively working H₂ sensor incorporating a CuO-reduced graphene oxide, i.e., CuO-rGO sandwiched nanostructure. Results show a time-dependent response and recovery of the sensor toward a hydrogen pulse, from 0 to 10, 50, 100, 500, 1000, and 1500 ppm. The response and recovery times were smaller than 80 and 60 s [96]. In a paper by Kaur et al., reduced graphene oxide (rGO) was utilized to improve the temperature-dependent selective H₂ sensing characteristics of Pd-doped WO₃. Sensing parameters as sensor response and reduced optimum working temperature were improved by incorporating differing amounts of graphite oxide (GO) into the basic composite (1.5 mol% Pd-doped WO₃). The sensor incorporating only 1 wt % rGO nanocomposite showed a significantly enhanced selective response to hydrogen (at 150 °C). The improvement in sensing response at a markedly reduced optimum operable temperature was assumed to be resulting from two factors: availability of a large specific surface area and excellent conductivity of rGO and the existence of heterojunctions at the rGO / Pd-doped WO₃ interface [97].

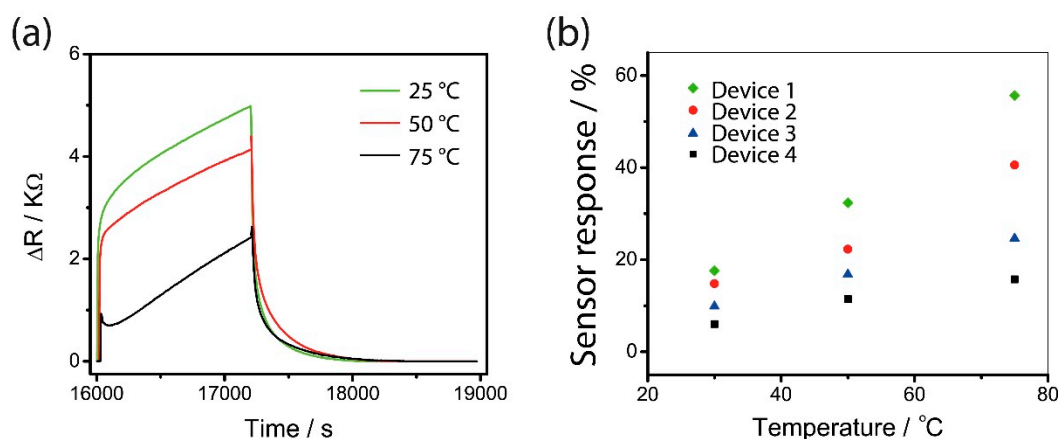


Figure 6. (a) Resistance response of Pd-rGO device to 3300 ppm hydrogen at different temperature; (b) Sensor response as a function of temperature for the data in (a) [89]. Copyright (2020), with permission from Elsevier.

Du et al. produced a hydrogen gas sensor consisting of graphene oxide/SiO₂/Si (Pd-rGO/SiO₂/Si) Schottky junction using a transfer printing method. GO and rGO layers were additionally decorated with Pd nanoparticles. An ultra high response of 970% was attained due to the presence of the junction, which was working under a reverse bias at room temperature. The sensor was capable to detect 0.16% H₂. This is much better than the response given by graphene-based resistance-type H₂ sensors at room temperature [98]. Similarly, Huang et al. synthesized graphene oxide/Pd/porous silicon and utilized it as H₂ sensitive material. Sensors based on this material can detect hydrogen at the level of 200 ppm in air (at 15 °C). The assumed sensing mechanism was based on the formation of palladium hydride and the creation of new electron pathways what led to electric resistance changes of the sensing material [99]. In a paper by Ma et al., a multilayer graphene film was transferred onto the capillary

to form a microcavity. A miniature fiber-optic H₂-sensor with a low detection limit of ~20 ppm and a short response time of 18 s was fabricated by incorporating of Pd-decorated graphene. Fast H₂ dissociation and an effective conversion of Pd lattice expansion into optical output are facilitated by tailoring the thickness to the level of nanometers. The manufacturing process let to provide a large surface-to-volume ratio of Pd/multilayer graphene [100].

Shin et al. describes another concept, basing on electrodeposition of flower-looking Pd nanoclusters (FPNCs) on CVD-originated graphene (CG) [101]. The sensitivity and response time of these sensors enhance upon the increasing FPNC concentration. In particular, the FPNCs_CG_H electrode has a minimum detectable level (MDL) of 0.1 ppm H₂. This paper demonstrates a facile fabrication manner of flower-like metal-graphene composites with the concentration control of flower-like domains. However, a combination of Pd–Pt possesses better hydrogenation properties in comparison to Pd alone. Kumar et al. employed Pd–Pt alloy in form of nanoparticles (NP) and synthesized aNP–G composite sensing layers for H₂ detection at temperatures ranging from –100 to 100 °C. The improvement of sensing parameters like the maximum sensitivity and response time at 20–40 °C was found to be consistent with the temperature dependence of hydrogen physisorption and chemisorption [102]. The parameters of all mentioned hydrogen gas sensors based on graphene, graphene derivatives, and various metals are summarized and listed in Table 2.

Table 2. Comparison of the H₂ sensors based on graphene and their composites with metals.

Sensor Material	Detection Level/Range	Operating Temperature	Response Time	Recovery Time	Ref.
PdNPs/GR	0.1–1%	RT	~30 s	–	[72]
Pt/GR	1%	RT–175 °C	–	–	[73]
Pt/RGO	40–40,000 ppm	RT	–	–	[74]
Pt/GR	1%	RT–100 °C	~65 s	–	[75]
Pt/GR	0.06–1%	22–100 °C	–	–	[76]
Pt/GR	1%	RT	–	–	[77]
Pt/GR	4 vol%	RT	~9 min	–	[78]
PtNPs/GR	1.6%	RT	0.97 s	0.92 s	[79]
Pt/RGO	0.5%	50 °C	63 s	104 s	[80]
Pt/GR	10 ² –10 ⁴ ppm	RT, 40 °C	–	–	[81]
Pt/GR	1%	160 °C	–	–	[82]
Pd/GNRs	1000 ppm	RT	60 s	90 s	[83]
Pd/GR	0.5–1%	RT	–	–	[84]
Pd/MLGN	40–8000 ppm	20–100 °C	3–8 s	7–35 s	[85]
Pd/SLG	1000 ppm	RT	–	–	[86]
Pt/RGO	1–100 ppm	RT	–	–	[87]
Pd/GR	0.0025–1%	RT	213 s	463 s	[88]
Pd/RGO	3300 ppm	30–75 °C	700–1000 s	–	[89]
Pd/GR	1%	RT	–	–	[90]
PtNPs/GR	1–1000 ppm	RT	–	–	[91]
Pd/GR	6–1000 ppm	RT	–	–	[92]
Ni–Pd/GR	1–1000 ppm	RT	–	–	[93]
Pd–Ag/GR	1000 ppm	70–190 °C	–	–	[94]
Pd–ZnO/RGO	1 ppb–500 ppm	50 °C	–	–	[96]
Pd–WO ₃ /RGO	50 ppm	150–350 °C	–	–	[97]
Pd/RGO	0.16%	RT	–	–	[98]
Pd/GO	200–2000 ppm	RT	10 min	20 min	[99]
Pd/GR	~20 ppm	RT	~18 s	–	[100]
Pd/GR	0.1–100 ppm	RT	–	–	[101]
Pd–Pt/GR	2%	–50–100 °C	<2 s	18 s	[102]

where: GR—graphene; RGO—reduced graphene oxide; NPs—nanoparticles; GNRs—graphene nanoribbons; MLGN—multi-layer graphene nanoribbon; SLG—single layer graphene; ppm—parts per million; RT—room temperature.

2.3.3. Graphene-Metal Oxide Nanocomposite

In the last two decades, different metal oxides, like ZnO, CeO₂, CuO, IrO₂, NiO, and SnO₂, were explored as active materials for hydrogen sensors [52,103–109]. In metal-oxides-based hydrogen sensors, the change in resistance upon the contact with reducing gas molecules (including H₂). One of the disadvantages metal oxide resistive sensors is their limited selectivity towards different reducing gases (including H₂). The second main drawback is a high operation temperature which may be as high as 200–400 °C. Substantial activation energy is required to trigger the oxidation of reducing gases under detection [110]. Thus, there is to eliminate the drawbacks by fabrication of a new class of materials. A reduced operational temperature as well as better selectivity may significantly increase the number of potential applications. The use of composites with multiple components seems to be potentially useful methodology for the fabrication of a new class of advanced hydrogen sensor.

The enhancement of the H₂ sensing performance of semiconductor metal oxide sensors may be achieved by different strategies, including the application of 1D nanostructures like nanotubes, nanowires, and nanorods [27,52,105]. Another progressive strategy relies on the utilization of metal oxide-carbon nanomaterials hybrids [51,111]. In particular, the incorporation of carbon nanostructures, such as carbon nanotubes (CNTs) described in Section 2.2. or graphene described in this section, in H₂-sensing devices seems to be a promising approach. Such research attempts try to combine selected unique electronic, catalytic and structural properties of the materials to be incorporated in a gas sensor. In addition to its high electronic conductivity, graphene may have a very well developed large surface area (multiple larger as that of multiwalled carbon nanotubes). Other positive features are structural flexibility and low electrical noise as a result of its 2D crystal lattice (extremely favorable for gas-sensing applications) [112]. However, it has to be stated once again the pristine graphene is not sensitive to hydrogen [113]. Graphene oxide (GO) or reduced graphene oxide (rGO) can be an alternative, due to their presumed good adsorption sites [85,114]. Moreover, the use of nanocomposites based on metal oxides and graphene for H₂ sensing is relatively unexplored.

Metal-oxide semiconductor nanomaterials like SnO₂ are considered to be one of the most promising candidates for sensing material, thanks to their wide band gap (3.6 eV, at 300 K) and high sensitivity. Compared with other semiconductors, SnO₂ nanomaterial has better gas detecting features, so it has been frequently applied for composite fabrication with graphene [115]. Various methods of creating these sorts of compounds have been reported in recent years. For example, to resolve the problem of the high working temperature of hydrogen sensors, in a paper by Munasinghe et al. SnO₂ nanowires were combined with graphene oxide (GO) to form a heterojunction [116]. Hydrogen sensing with heteronanostructures based on reduced graphene oxide and tin oxide is also investigated in an article by Russo et al. [117]. In another paper, by Zhang et al., sensing material, based on graphene as well, was hydrothermally synthesized to obtain SnO₂-graphene (S-G) composites for H₂ sensing at a low operating temperature. The probable growth mechanisms of the radial flower-looking SnO₂ domains and S-G composites are proposed [118]. Moreover, Dhall et al. has proven that the specific form of Pd and SnO₂ domains (isolated nanoparticles) on graphene ensured improved sensitivity and selectivity towards H₂, which was superior to typical chemiresistive gas sensors [119]. Esfandiar et al. used rGO in order to enhance sensing properties towards hydrogen of Pd-decorated TiO₂ nanoparticles [120] and Pd-WO₃ [121]. Outstanding sensitivity of 92% and spectacularly short response time ca. 20 s were noticed for experiments with 500 ppm of H₂ at 180 °C. Furthermore, the Pd-WO₃/RGO-based gas sensor was sensitive to a 20 ppm concentration of hydrogen gas at room temperature. Hen et al., also describe a hydrogen sensor containing Pd and WO₃ (Figure 7) [122]. The device, when exposed to the hydrogen (4 vol% H₂/Ar mixed gas), confirms that the short-circuit current and open-circuit voltage nearly disappear (Figure 8a) due to the gasochromic Pd-WO₃ film being colored. Figure 8b demonstrates the detailed response of the device to the hydrogen gas, where it is set to be illuminated by the 980 nm laser of 10 mW. Furthermore, as shown in Figure 8c, the device can repeat effectively.

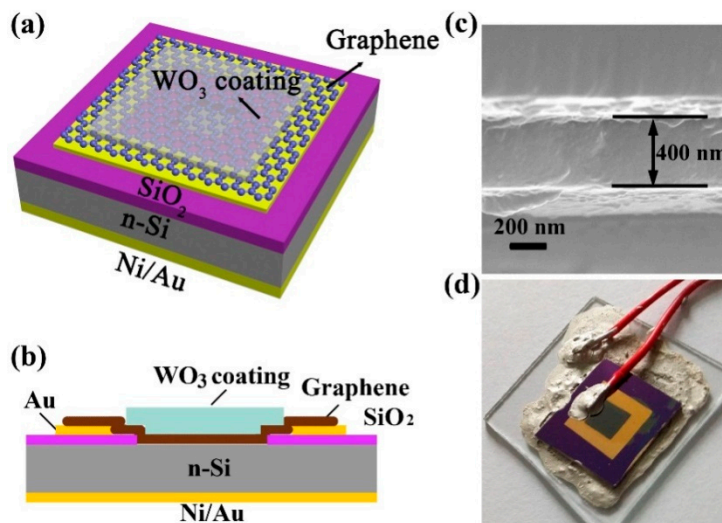


Figure 7. Device architecture of the tandem gasochromic-Pd-WO₃/graphene/Si optoelectronic hydrogen sensor. (a) Tilted schematic device structure; (b) Cross-sectional schematic structure; (c) Cross-sectional SEM image; (d) Optical photograph of a produced device [122]. Copyright (2020), with permission from Elsevier.

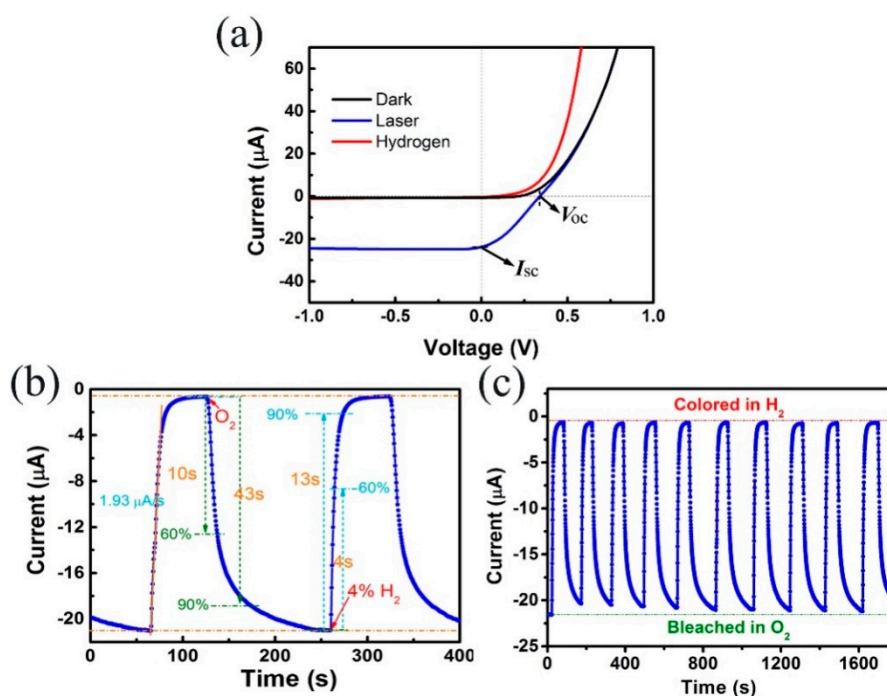


Figure 8. Tandem gasochromic-Pd-WO₃/graphene/Si device for optoelectronic hydrogen sensors. (a) I-V curves of the device in darkness and under 10 mW laser illumination, with and without H₂; (b) Response of the device to the 4 vol% H₂/Ar; (c) Cyclic performance of the device [122]. Copyright (2020), with permission from Elsevier.

Zinc oxide itself is historically one of the most common metal oxides that has been widely explored in chemical sensors. ZnO attracted the attention of research due to several useful properties, such as good conductivity, low toxicity, and good thermal stability. Many fabrication/modification/utilization scenarios have been elaborated in order to ensure the highest sensitivity and selectivity of ZnO. The addition of noble metals is a typical modification route along with adjusting of the optimal operating temperature [123]. A highly sensitive and selective H₂ sensor of rGO and ZnO nanofibers, fabricated using a low-cost and versatile electrospinning process is reported by Abidden et al. [124].

Singh et al., report that ZnO-decorated luminescent graphene acts as a potential gas sensor at room temperature, in which reduced graphene oxide acts as a highly conductive mesh in gas sensing [125]. Anand et al. describe the incorporation of graphene into ZnO nanorods for high-efficiency hydrogen sensing applications. Authors suggest that the optimum amount of graphene for the creation of a rGO/ZnO nanocomposite hydrogen sensor is 1.2 wt %. From Figure 9 it is obvious that RGO/ZnO based gas sensor has a quicker response and shorter recovery time as compared to bare ZnO based sensor [126]. In the paper by Tebarez et al. relative humidity is shown to be a critical factor for the performance of H₂ sensors based on rGO/aluminum zinc oxide, which suggests the need for more controlled in-situ experiments for a proper calibration of these devices [127]. Drmoseh et al. investigate a long term stability and selectivity test of a ZnO, rGO/ZnO, Au/rGO/ZnO sensor towards 500 ppm of H₂ with and without UV irradiation at room temperature (Figures 10 and 11) the detailed gas sensing mechanism being shown on Figure 12 [128]. In a different work by Liu et al., the authors present a novel method for the large-scale production of hybrid semiconducting metal oxide-graphene nanostructures by floating graphene sheets on the surface of a solution [129]. Huang et al. report that ZnO nanorods (NRs) were grown using sol-gel/hydrothermal methods on SiO₂, carbon nanotubes (CNT)/SiO₂, and graphene/SiO₂ substrates to fabricate H₂ sensitive chips. Results indicate that ZnO NRs/CNT/SiO₂ structures exhibit better H₂ sensing performance than the other two types of ZnO NRs-based structures [130].

Besides the more common graphene modifications with SnO₂ or ZnO, papers can also be found where authors examine the influence of In₂O₃, TiO₂, NiO, LiTaO₃, ZnFe₂O₄, and CuO modifiers on H₂ sensing [55,131–135]. Mansha et al. present the synthesis of an In₂O₃/graphene heterostructure and its hydrogen gas sensing properties. The synthesized materials exhibited good sensitivity, ranging from 250 to 2000 ppm at 250 °C. The better sensitivity and slower recovery time of the heterostructure sensor are attributed to a reduction in the band gap achieved by the addition of graphene layers [55]. A sensor containing p-TiO₂/n-graphene that prompted hydrogen sensing in the temperature range of 75–150 °C is presented by Dutta et al. [131]. In another paper, a high-performance NiO-decorated graphene sensor showed high repeatability, high response, and excellent recovery properties with a powerful response behavior for increasing H₂ concentration in a relatively low working temperature (200 °C) compare to pristine NiO [132]. In an article by Zhang et al., a CuO-reduced graphene oxide sandwiched nanostructure is described with its hydrogen sensing characteristics, where response and recovery times of less than 80 and 60 s were observed [133]. Using graphene-like nano-sheets deposited on lithium tantalate (LiTaO₃) for H₂ sensing gave a response time that in 90% of cases was 12 s of 0.125% and a recovery time that was less than 1 min [134]. Among them, spinel ferrites with a chemical composition of MFe₂O₄ (M = Cu, Co, Mn, Zn, etc.) have shown themselves to be especially promising, and semiconducting properties were displayed by the majority of spinel ferrites with two different cationic species occupying the complex voids. Achary et al. report efficient synthesis of rGO-ZnFe₂O₄-Pd nanocomposites via a rapid and microwave route. The designed nanocomposite was sensitive to H₂ in a wide range of concentrations. The structural tuning of reduced graphene oxide with ZnFe₂O₄ and Pd nanoparticles was performed aiming at the design of an effective H₂ sensing material. Such based H₂ sensor ensures high sensitivity with a short response/recovery times, and reversibility towards H₂. The sensing mechanism is depicted on Figure 13 [135]. The parameters of all mentioned hydrogen gas sensors based on graphene, graphene derivatives, and various metal oxides are summarized and listed in Table 3.

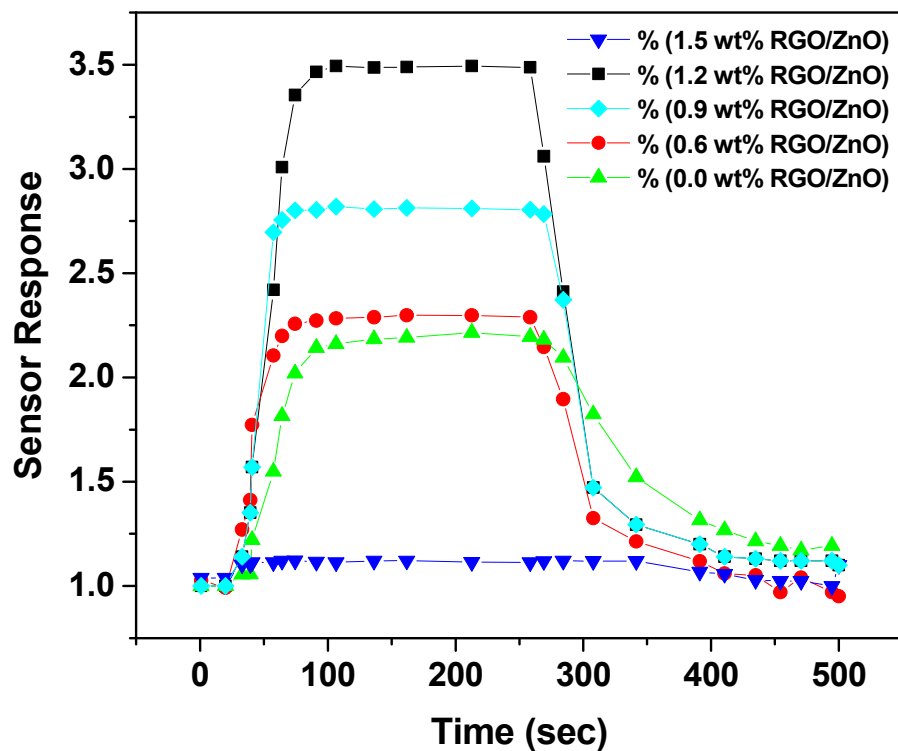


Figure 9. Sensor response vs time graph for ZnO and RGO/ZnO sensors towards 200 ppm of hydrogen at their respective optimum operating temperatures, i.e., 400 °C for ZnO and 150 °C for RGO/ZnO composite [126]. Copyright (2020), with permission from Elsevier.

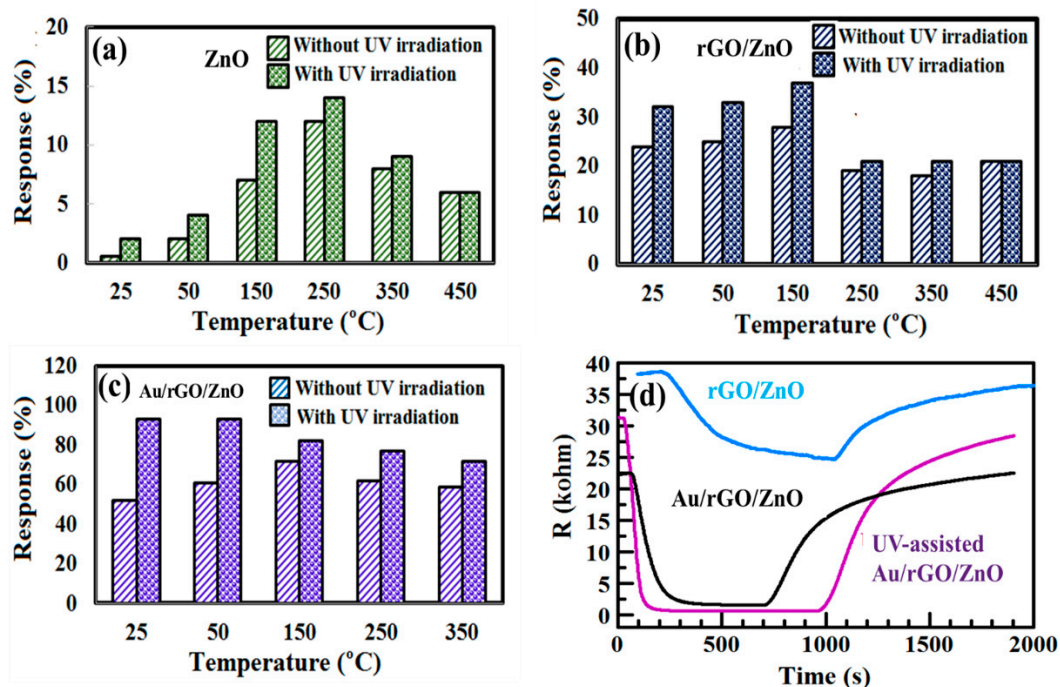


Figure 10. (a–c) Responses at different temperatures of ZnO, rGO/ZnO, and Au/rGO/ZnO sensor with and without UV irradiation; (d) Dynamic response at room temperature of rGO, Au/rGO/ZnO, and UV assisted Au/rGO/ZnO [128]. Copyright (2020), with permission from Elsevier.

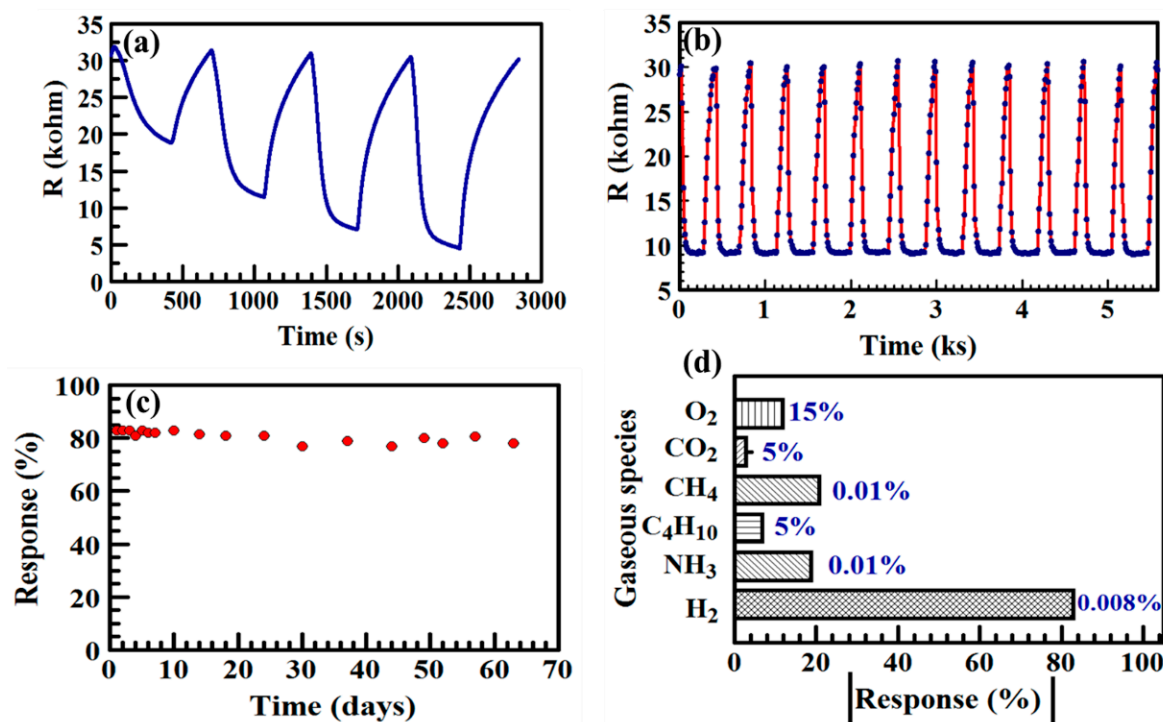


Figure 11. (a) Dynamic response curve of different hydrogen concentrations; (b) Repeatability measurements of the Au/rGO/ZnO sensor toward 300 ppm of H₂; (c,d) long term stability, and selectivity test of Au/rGO/ZnO sensor toward 500 ppm of H₂, tests were realized at room temperature and under UV irradiation [128]. Copyright (2020), with permission from Elsevier.

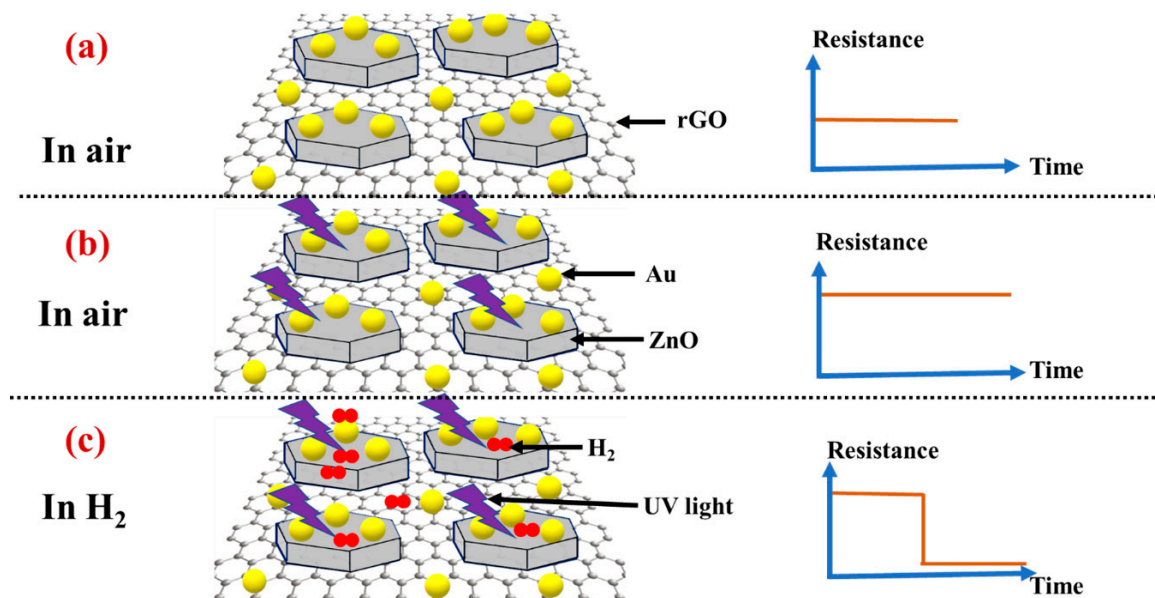


Figure 12. Gas sensing mechanism of Au/rGO/ZnO sensor in (a) air (b) air with UV light, and (c) H₂ environment with UV irradiation [128]. Copyright (2020), with permission from Elsevier.

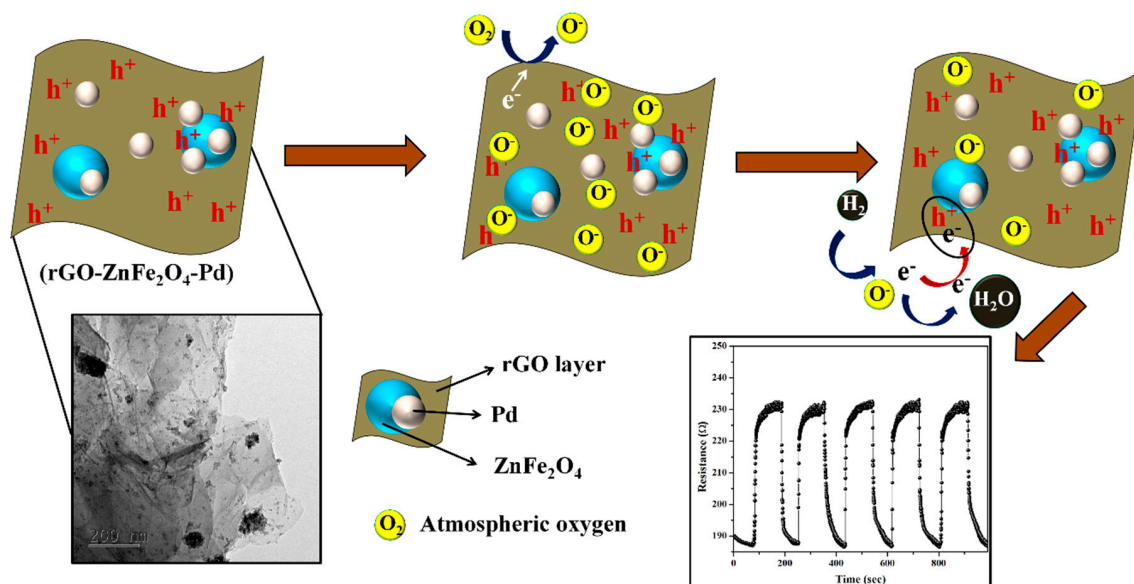


Figure 13. Schematic representation of sensing mechanism [135]. Copyright (2020), with permission from Elsevier.

Table 3. Comparison of the H₂ sensors based on graphene and their composites with metal oxides.

Sensor Material	Detection Level/Range	Operating Temperature	Response Time	Recovery Time	Ref.
SnO ₂ /GR	100 ppm	50 °C	—	—	[115]
SnO ₂ /GO	20–100 ppm	20–150 °C	—	—	[116]
Pd-SnO ₂ /RGO	0.5–3%	RT	3–7 s	2–6 s	[117]
SnO ₂ /GR	100%	150 °C	—	—	[118]
Pd-SnO ₂ /GR	2%	25–200 °C	—	—	[119]
Pt or Pd-TiO ₂ /RGO	100–10,000 ppm	RT	<1 min	<1 min	[120]
Pd-WO ₃ /RGO	20–10,000 ppm	RT–250 °C	<1 min	<1 min	[121]
Pd-WO ₃ /GR	0.05 vol%	RT	13 s	43 s	[122]
ZnO/RGO, SnO ₂ /RGO	10 ppm	300–450 °C	—	—	[124]
ZnO/GR	200 ppm	100–150 °C	22–96 s	90–190 s	[126]
ZnO/RGO	30–160 ppm	RT	—	—	[127]
ZnO/RGO	500 ppm	RT	8 s	612 s	[128]
ZnO/GR	0.06–1%	RT	—	—	[129]
ZnO/CNT/GR	1000 ppm	300 °C	—	—	[130]
TiO ₂ /GR	0.5%	75–150 °C	16 s	61 s	[131]
NiO/GR	400–2000 ppm	100–350 °C	—	—	[132]
CuO/RGO	50–1500 ppm	RT	80 s	60 s	[133]
LiTaO ₃ /GR	1%	RT–40 °C	<1 min	10 min	[134]
GR	50–1000 ppm	25–100 °C	18 s	9 s	[135]

where: GR—graphene; RGO—reduced graphene oxide; GO—graphene oxide; ppm — parts per million; RT—room temperature.

3. Summary

In this article, we have reviewed the recent literature on hydrogen sensors based on different sensing materials with particular attention paid to the application of graphene and its derivatives. Plenty of various parameters (molecular reactivity, interface accessibility, chemical and mechanical durability, and electrical robustness) may influence sensing performance of hydrogen detectors. With ongoing technological developments in the area of sensors, researchers have been greatly preoccupied with the progress of hydrogen gas sensors. Advanced sensing systems demand methods and devices which should be controlled online and offer a fast and sensitive response. Cost effectiveness is a crucial issue as well. Also, the performance of a chemical sensor should be stable and basically

independent on temperature, humidity, and other interfering substances. The explosive nature of H_2 gas urges detection at low levels of concentration. Thus, hydrogen should be detected at ppm/ppb level which is associated to hydrogen installation leakages to avoid explosion hazards. Upon the time passed, various hydrogen detection principles and materials became well explored. This current article has reviewed what materials have been used for detection, what techniques have enhanced performance, as well as reviewing ppb level detection studies for H_2 gas. Predominating part of literature announcement concentrate on the development of H_2 gas sensors with a shortened response/recovery time, high selectivity, and extended stability. Hydrogen's volatile character and the ability to penetrate some solids implies the necessity of constant monitoring of H_2 presence. Thus, room operation temperature is welcome due to the reduction of energy consumption. This would clearly minimize calamity risk.

Due to the two-dimensional nature of graphene, nearly every carbon atom in a graphene sheet lays on the surface and, as a result, each such carbon atom may contribute to interaction with chemical species in the gas phase. This feature of graphene can be considered to be responsible for its outstanding sensing behavior in the presence of some gases including hydrogen. Even lowest-level detection capability may be expected, finally reaching the level of a single molecule. Further, the ease of functionalizing graphene, either by a chemical manner (preparative adsorption of surface modifying substances) or by a physical manner (electrical and pressure treatments), enables engineering of electronic properties, which in turn may help to solve to the selectivity issue in fact the crucial problem of chemical sensors. Endowed with a large surface area, chemically/catalytically reactive centers, and steerable chemical and electronic features, graphene derivatives like graphene oxide GO and reduced graphene oxide rGO have several valuable properties as potential gas sensing material or a platform for further surface engineering. Engineered graphene/graphene derivatives may have a proven advantage over pristine metal oxides, carbon nanotubes, and conductive polymers. Even though both carbon-based nanomaterials such as CNTs and graphene exhibit specific electrical properties that suit them for H_2 gas sensing. Some of sensing properties like enhanced sensing features of graphene originated sensing materials over CNTs can be attributed to the high accessibility of the graphene surface (sensing surface), which is greater than that of CNTs. The introduction of the chemically active functionalities was usually performed aiming to enhancement of the detection level, shortening of response/recovery time in room conditions (key sensing parameters for a H_2 detection device). The spectacular progress in sensing parameters as compared to unmodified graphene are resulting from the synergy of individual features of graphene and modifiers. There is great potential in graphene originated hybrids comprising graphene, graphene derivatives, metal and metal oxide domains, and polymers. The conclusion is supported by large amounts of research projects dealing with detecting a wide range of H_2 concentrations and temperatures aiming at enhanced sensing response and high selectivity.

Theoretically, any progress of graphene originated hydrogen sensors envisages graphene as being able to fulfill most hydrogen sensor requirements even regarding the needs of industrial applications. Selectivity to hydrogen is the most compelling issue for graphene-based sensors because some substances (like CO, CH_4 , and NH_3) exhibit reductive properties, which usually cause some cross-response. The application of graphene and its derivatives in sensing hydrogen gas belongs to the newest research trends in chemical sensing. This trend is a result of the general popularity of graphene, hailed as the material of the future; however, we also owe it to several exceptional features offered by this emerging sensing material. To begin, one may put forward steerable conductivity, evident chemical stability, and insertion of heteroatoms ranging from nitrogen and phosphorus to noble/transition metals like platinum. Additionally, graphene is susceptible to 3D structuring and fabrication of hybrid materials, including polymer blends. Thus, a broad scope of parameters may be manipulated to achieve the desired sensing performance toward hydrogen gas. Although the application of graphene for H_2 sensing purposes is still in the stage of intensive laboratory tests, some advantages and drawbacks are already apparent. Several important achievements presented

in studies can be quoted as: (i) lowering the operational temperature to room temperature (in some cases), (ii) linearity of the hydrogen detection characteristic, i.e., output signal is linearly dependent on hydrogen concentration, (iii) partly adjustable sensing range, (iv) limitation of cross-sensitivities, and (v) relative ease of manufacturing.

As mentioned, the current state of research in the area of hydrogen gas sensing by graphene-based devices can be described as the laboratory testing level. Consequently, the technology being under development may be considered its main drawback. Most research announcements fail to deliver adequate information on the chemical stability of graphene-based materials working in the particular conditions required by chemical processes that occur in the sensing layer. Strongly exothermic oxidation of hydrogen is one of them. Usually sensing performance stability is not tested and is therefore unknown in general. At the current state of knowledge, graphene-based hydrogen gas sensors cannot compete with those commercially available, which are still mostly based on modified semiconductor metal oxides. These sensors have a long application history behind them and the stability problem has already been properly addressed by existing manufacturing and exploitation technologies. Nevertheless, this situation should encourage the sensor research community to focus on the issue of stability in future works, rather than to abandon the subject.

Author Contributions: Conceptualization A.I. and J.P.L.; writing—original draft preparation A.I. (most of the text) and J.P.L. (instruction and summary in half); writing—review and editing A.I. and J.P.L.; supervision A.I. and J.P.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Korotcenkov, G. *Chemical Sensors: Comprehensive Sensor Technologies Volume 5: Electrochemical and Optical Sensors*; Momentum Press: New York, NY, USA, 2011.
2. Hulanicki, A.; Glab, S.; Ingman, F. Chemical sensors: Definitions and classification. *Pure Appl. Chem.* **1991**, *63*, 1247–1250. [CrossRef]
3. Scipioni, A.; Manzardo, A.; Ren, J. *Hydrogen Economy: Supply Chain, Life Cycle Analysis and Energy Transition for Sustainability*; Academic Press: Cambridge, MA, USA, 2017.
4. Hydrogen Isn't the Fuel of the Future. It's Already Here. Available online: <https://www.weforum.org/agenda/2019/06/the-clean-energy-of-the-future-is-already-here/> (accessed on 17 May 2020).
5. Ramachandran, R.; Menon, R.K. An overview of industrial uses of hydrogen. *Int. J. Hydrogen Energy* **1998**, *23*, 593–598. [CrossRef]
6. Dos Santos, M.C.; Maynard, M.C.; Aveiro, L.R.; Da Paz, E.C.; Pinheiro, V.D.S. Carbon-Based Materials: Recent Advances, Challenges, and Perspectives. *Ref. Modul. Mater. Sci. Mater. Eng.* **2017**. [CrossRef]
7. 60 Uses of Graphene—The Ultimate Guide to Graphene's (Potential) Applications 2016. Available online: <https://nanografi.com/blog/60-uses-of-graphene/> (accessed on 17 May 2020).
8. Lukaszewicz, J.P. Carbon Materials for Chemical Sensors: A Review. *Sens. Lett.* **2006**, *4*, 53–98. [CrossRef]
9. Lukaszewicz, J.P. Carbon Films for Humidity Sensors. *Sens. Lett.* **2006**, *4*, 281–304. [CrossRef]
10. Figueiredo, J.L.; Pereira, M.C.; Freitas, M.M.; Órfão, J. Modification of the surface chemistry of activated carbons. *Carbon* **1999**, *37*, 1379–1389. [CrossRef]
11. Yadav, R.; Dixit, C. Synthesis, characterization and prospective applications of nitrogen-doped graphene: A short review. *J. Sci. Adv. Mater. Devices* **2017**, *2*, 141–149. [CrossRef]
12. Shafeeyan, M.S.; Daud, W.M.A.W.; Houshmand, A.; Shamiri, A. A review on surface modification of activated carbon for carbon dioxide adsorption. *J. Anal. Appl. Pyrolysis* **2010**, *89*, 143–151. [CrossRef]
13. Dinh, N.X.; Van Quy, N.; Huy, T.Q.; Le, A.-T. Decoration of Silver Nanoparticles on Multiwalled Carbon Nanotubes: Antibacterial Mechanism and Ultrastructural Analysis. *J. Nanomater.* **2015**, *2015*, 1–11. [CrossRef]
14. Cyganiuk, A.; Klimkiewicz, R.; Olejniczak, A.; Lukaszewicz, J.P. Biotechnological fabrication of LaMnO₃-carbon catalyst for n-butanol conversion to ketones. *Carbon* **2010**, *48*, 99–106. [CrossRef]

15. Cyganiuk, A.; Klimkiewicz, R.; Bumajdad, A.; Ilnicka, A.; Lukaszewicz, J.P. Nanostructured composite TiO₂/carbon catalysts of high activity for dehydration of n-butanol. *Mater. Sci. Eng. B* **2015**, *198*, 35–42. [CrossRef]
16. Zhang, J.; Shan, G.-C. Stacking control in graphene-based materials: A promising method for fascinating physical properties. *Front. Phys.* **2018**, *14*, 23301. [CrossRef]
17. Pal, A.N.; Ghosh, A. Ultralow noise field-effect transistor from multilayer graphene. *Appl. Phys. Lett.* **2009**, *95*, 82105. [CrossRef]
18. Gayathri, S.; Jayabal, P.; Kottaisamy, M.; Ramakrishnan, V. Synthesis of few layer graphene by direct exfoliation of graphite and a Raman spectroscopic study. *AIP Adv.* **2014**, *4*, 27116. [CrossRef]
19. Kamedulski, P.; Ilnicka, A.; Lukaszewicz, J.P. Selected Aspects of Graphene Exfoliation as an Introductory Step Towards 3D Structuring of Graphene Nano-Sheets. *Curr. Graphene Sci.* **2019**, *2*, 106–117. [CrossRef]
20. Taguchi, N. Gas Detecting Element and Method of Making It. U.S. Patent US3695848A, 22 February 1972.
21. Ihokura, K.; Watson, J. *The Stannic Oxide Gas Sensor Principles and Applications*; CRC Press: Boca Raton, FL, USA, 1994.
22. Chen, W.; Zhou, Q.; Wan, F.; Gao, T. Gas Sensing Properties and Mechanism of Nano-SnO₂-Based Sensor for Hydrogen and Carbon Monoxide. *J. Nanomater.* **2012**, *2012*, 1–9. [CrossRef]
23. Cui, Y.; Wei, Q.; Park, H.; Lieber, C.M. Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species. *Science* **2001**, *293*, 1289–1292. [CrossRef]
24. Wisitsora-At, A.; Tuantranont, A.; Comini, E.; Sberveglieri, G.; Wlodarski, W. Characterization of n-type and p-type semiconductor gas sensors based on NiOx doped TiO₂ thin films. *Thin Solid Films* **2009**, *517*, 2775–2780. [CrossRef]
25. Lee, J.H.; Kwak, S.; Lee, J.-H.; Kim, I.; Yoo, Y.K.; Lee, T.H.; Shim, Y.-S.; Kim, J.; Lee, K.H. Sputtered PdO Decorated TiO₂ Sensing Layer for a Hydrogen Gas Sensor. *J. Nanomater.* **2018**, *2018*, 1–8. [CrossRef]
26. Nakate, U.T.; Ahmad, R.; Patil, P.; Yu, Y.; Hahn, Y.-B. Ultra thin NiO nanosheets for high performance hydrogen gas sensor device. *Appl. Surf. Sci.* **2020**, *506*, 144971. [CrossRef]
27. Raza, M.H.; Kaur, N.; Comini, E.; Pinna, N. Toward Optimized Radial Modulation of the Space-Charge Region in One-Dimensional SnO₂-NiO Core-Shell Nanowires for Hydrogen Sensing. *ACS Appl. Mater. Interfaces* **2020**, *12*, 4594–4606. [CrossRef] [PubMed]
28. Vomiero, A.; Ferroni, M.; Comini, E.; Faglia, G.; Sberveglieri, G. Preparation of Radial and Longitudinal Nanosized Heterostructures of In₂O₃ and SnO₂. *Nano Lett.* **2007**, *7*, 3553–3558. [CrossRef]
29. Thai, N.X.; Van Duy, N.; Van Toan, N.; Hung, C.M.; Van Hieu, N.; Hoa, N.D. Effective monitoring and classification of hydrogen and ammonia gases with a bilayer Pt/SnO₂ thin film sensor. *Int. J. Hydrogen Energy* **2020**, *45*, 2418–2428. [CrossRef]
30. Wu, C.-H.; Zhu, Z.; Chang, H.-M.; Jiang, Z.-X.; Hsieh, C.-Y.; Wu, R.-J. Pt@NiO core-shell nanostructure for a hydrogen gas sensor. *J. Alloy. Compd.* **2020**, *814*, 151815. [CrossRef]
31. Kumar, A.; Sanger, A.; Kumar, A.; Chandra, R. Porous silicon filled with Pd/WO₃-ZnO composite thin film for enhanced H₂ gas-sensing performance. *RSC Adv.* **2017**, *7*, 39666–39675. [CrossRef]
32. Wang, C.; Yin, L.; Zhang, L.; Xiang, N.; Gao, R. Metal Oxide Gas Sensors: Sensitivity and Influencing Factors. *Sensors* **2010**, *10*, 2088–2106. [CrossRef]
33. Gu, H.; Wang, Z.; Hu, Y. Hydrogen Gas Sensors Based on Semiconductor Oxide Nanostructures. *Sensors* **2012**, *12*, 5517–5550. [CrossRef]
34. Sitarz, M.; Kwoka, M.; Comini, E.; Zappa, D.; Szuber, J. Surface chemistry of SnO₂ nanowires on Ag-catalyst-covered Si substrate studied using XPS and TDS methods. *Nanoscale Res. Lett.* **2014**, *9*, 43. [CrossRef]
35. Trung, D.D.; Hoa, N.D.; Van Tong, P.; Van Duy, N.; Dao, T.; Chung, H.; Nagao, T.; Van Hieu, N. Effective decoration of Pd nanoparticles on the surface of SnO₂ nanowires for enhancement of CO gas-sensing performance. *J. Hazard. Mater.* **2014**, *265*, 124–132. [CrossRef]
36. Helwig, A.; Müller, G.; Sberveglieri, G.; Faglia, G. Catalytic enhancement of SnO₂ gas sensors as seen by the moving gas outlet method. *Sens. Actuators B Chem.* **2008**, *130*, 193–199. [CrossRef]
37. Available online: <http://www.figarosensor.com/> (accessed on 17 May 2020).
38. Gaiardo, A.; Fabbri, B.; Guidi, V.; Bellutti, P.; Giberti, A.; Gherardi, S.; Vanzetti, L.; Malagù, C.; Zonta, G. Metal Sulfides as Sensing Materials for Chemoresistive Gas Sensors. *Sensors* **2016**, *16*, 296. [CrossRef] [PubMed]

39. Gottam, S.R.; Tsai, C.-T.; Wang, L.-W.; Wang, C.-T.; Lin, C.-C.; Chu, S.-Y. Highly sensitive hydrogen gas sensor based on a MoS₂-Pt nanoparticle composite. *Appl. Surf. Sci.* **2020**, *506*, 144981. [[CrossRef](#)]
40. Guidi, V.; Fabbri, B.; Gaiardo, A.; Gherardi, S.; Giberti, A.; Malagù, C.; Zonta, G.; Bellutti, P. Metal Sulfides as a New Class of Sensing Materials. *Procedia Eng.* **2015**, *120*, 138–141. [[CrossRef](#)]
41. Zhang, L.; Jiang, H.; Zhang, J.; Huang, Y.; Tian, J.; Deng, X.; Zhao, X.; Zhang, W. Flexible nanofiber sensor for low-concentration hydrogen detection. *Nanotechnology* **2019**, *31*, 015504. [[CrossRef](#)]
42. Cho, K.H.; Yu, H.; Lee, J.S.; Jang, J. Facile synthesis of palladium-decorated three-dimensional conducting polymer nanofilm for highly sensitive H₂ gas sensor. *J. Mater. Sci.* **2020**, *55*, 5156–5165. [[CrossRef](#)]
43. Sadek, A.Z.; Wlodarski, W.; Kalantar-Zadeh, K.; Baker, C.; Kaner, R. Doped and dedoped polyaniline nanofiber based conductometric hydrogen gas sensors. *Sens. Actuators A Phys.* **2007**, *139*, 53–57. [[CrossRef](#)]
44. Sakthivel, M.; Weppner, W. Response Behaviour of a Hydrogen Sensor Based on Ionic Conducting Polymer-metal Interfaces Prepared by the Chemical Reduction Method. *Sensors* **2006**, *6*, 284–297. [[CrossRef](#)]
45. Kim, D.-H.; Kim, S.-J.; Shin, H.; Koo, W.-T.; Jang, J.-S.; Kang, J.-Y.; Jeong, Y.J.; Kim, I.-D. High-Resolution, Fast, and Shape-Conformable Hydrogen Sensor Platform: Polymer Nanofiber Yarn Coupled with Nanograined Pd@Pt. *ACS Nano* **2019**, *13*, 6071–6082. [[CrossRef](#)]
46. Han, T.; Nag, A.; Mukhopadhyay, S.; Xu, Y. Carbon nanotubes and its gas-sensing applications: A review. *Sens. Actuators A Phys.* **2019**, *291*, 107–143. [[CrossRef](#)]
47. Kim, M.I.; Lee, Y.-S. A Comprehensive Review of Gas Sensors Using Carbon Materials. *J. Nanosci. Nanotechnology* **2016**, *16*, 4310–4319. [[CrossRef](#)] [[PubMed](#)]
48. Chauhan, P.S.; Bhattacharya, S. Hydrogen gas sensing methods, materials, and approach to achieve parts per billion level detection: A review. *Int. J. Hydrogen Energy* **2019**, *44*, 26076–26099. [[CrossRef](#)]
49. McConnell, C.; Kanakaraj, S.N.; Dugre, J.; Malik, R.; Zhang, G.; Haase, M.R.; Hsieh, Y.-Y.; Fang, Y.; Mast, D.; Shanov, V. Hydrogen Sensors Based on Flexible Carbon Nanotube-Palladium Composite Sheets Integrated with Ripstop Fabric. *ACS Omega* **2019**, *5*, 487–497. [[CrossRef](#)] [[PubMed](#)]
50. Dhall, S.; Jaggi, N. Hydrogen Gas Sensing Characteristics of Multiwalled Carbon Nanotubes Based Hybrid Composites. *J. Electron. Mater.* **2015**, *45*, 695–702. [[CrossRef](#)]
51. Dhall, S.; Sood, K.; Jaggi, N. A hydrogen gas sensor using a Pt-sputtered MWCNTs/ZnO nanostructure. *Meas. Sci. Technol.* **2014**, *25*, 085103. [[CrossRef](#)]
52. Dhall, S.; Jaggi, N. Room temperature hydrogen gas sensing properties of Pt sputtered F-MWCNTs/SnO₂ network. *Sens. Actuators B Chem.* **2015**, *210*, 742–747. [[CrossRef](#)]
53. Du, Y.G.; Zheng, H.X.; Ni, H. A Room-temperature Hydrogen Gas Sensor Using Palladium-decorated Single-Walled Carbon Nanotube/Si Heterojunction. *Mater. Sci.* **2016**, *22*, 209–212. [[CrossRef](#)]
54. Jung, D.; Han, M.; Lee, G.S. Fast-Response Room Temperature Hydrogen Gas Sensors Using Platinum-Coated Spin-Capable Carbon Nanotubes. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3050–3057. [[CrossRef](#)]
55. Mansha, M.; Qurashi, A.; Ullah, N.; Bakare, F.O.; Khan, I.; Yamani, Z.H. Synthesis of In₂O₃/graphene heterostructure and their hydrogen gas sensing properties. *Ceram. Int.* **2016**, *42*, 11490–11495. [[CrossRef](#)]
56. Wang, J.; Rath, S.; Singh, B.; Lee, I.; Joh, H.-I.; Kim, G.-H. Alternating Current Dielectrophoresis Optimization of Pt-Decorated Graphene Oxide Nanostructures for Proficient Hydrogen Gas Sensor. *ACS Appl. Mater. Interfaces* **2015**, *7*, 13768–13775. [[CrossRef](#)]
57. Zhang, Z.; Xue, Q.; Du, Y.; Ling, C.; Xing, W. Highly enhanced sensitivity of hydrogen sensors using novel palladium-decorated graphene nanoribbon film/SiO₂/Si structures. *J. Mater. Chem. A* **2014**, *2*, 15931–15937. [[CrossRef](#)]
58. Kuila, T.; Bose, S.; Mishra, A.K.; Khanra, P.; Kim, N.H.; Lee, J.H. Chemical functionalization of graphene and its applications. *Prog. Mater. Sci.* **2012**, *57*, 1061–1105. [[CrossRef](#)]
59. Wang, J.; Kwak, Y.; Lee, I.-Y.; Maeng, S.; Kim, G.-H. Highly responsive hydrogen gas sensing by partially reduced graphite oxide thin films at room temperature. *Carbon* **2012**, *50*, 4061–4067. [[CrossRef](#)]
60. Pavithra, A.; Rakkesh, R.A.; Durgalakshmi, D.; Balakumar, S. Room Temperature Detection of Hydrogen Gas Using Graphene Based Conductometric Gas Sensor. *J. Nanosci. Nanotechnol.* **2017**, *17*, 3449–3453. [[CrossRef](#)]
61. Shaban, M.; Ali, S.; Rabia, M. Design and application of nanoporous graphene oxide film for CO₂, H₂, and C₂H₂ gases sensing. *J. Mater. Res. Technol.* **2019**, *8*, 4510–4520. [[CrossRef](#)]
62. Zhang, L.-S.; Wang, W.D.; Liang, X.-Q.; Chu, W.-S.; Song, W.; Wu, Z.-Y. Characterization of partially reduced graphene oxide as room temperature sensor for H₂. *Nanoscale* **2011**, *3*, 2458–2460. [[CrossRef](#)] [[PubMed](#)]

63. Basu, S.; Hazra, S.K. Graphene—Noble Metal Nano-Composites and Applications for Hydrogen Sensors. *C J. Carbon Res.* **2017**, *3*, 29. [\[CrossRef\]](#)
64. Sharma, B.; Kim, J.-S. MEMS based highly sensitive dual FET gas sensor using graphene decorated Pd-Ag alloy nanoparticles for H₂ detection. *Sci. Rep.* **2018**, *8*, 5902. [\[CrossRef\]](#)
65. Varghese, S.S.; Lonkar, S.; Singh, K.; Swaminathan, S.; Abdala, A. Recent advances in graphene based gas sensors. *Sens. Actuators B Chem.* **2015**, *218*, 160–183. [\[CrossRef\]](#)
66. Meng, F.; Guo, Z.; Huang, X.-J. Graphene-based hybrids for chemiresistive gas sensors. *TrAC Trends Anal. Chem.* **2015**, *68*, 37–47. [\[CrossRef\]](#)
67. Yang, Y.; Li, S.; Yang, W.; Yuan, W.; Xu, J.; Jiang, Y. In Situ Polymerization Deposition of Porous Conducting Polymer on Reduced Graphene Oxide for Gas Sensor. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13807–13814. [\[CrossRef\]](#)
68. Zheng, Y.; Lee, D.; Koo, H.Y.; Maeng, S. Chemically modified graphene/PEDOT: PSS nanocomposite films for hydrogen gas sensing. *Carbon* **2015**, *81*, 54–62. [\[CrossRef\]](#)
69. Al-Mashat, L.; Shin, K.; Kalantar-Zadeh, K.; Plessis, J.D.; Han, S.H.; Kojima, R.W.; Kaner, R.B.; Li, D.; Gou, X.; Ippolito, S.J.; et al. Graphene/Polyaniline Nanocomposite for Hydrogen Sensing. *J. Phys. Chem. C* **2010**, *114*, 16168–16173. [\[CrossRef\]](#)
70. Zou, Y.; Wang, Q.; Xiang, C.; Tang, C.; Chu, H.; Qiu, S.; Yan, E.; Xu, F.; Sun, L. Doping composite of polyaniline and reduced graphene oxide with palladium nanoparticles for room-temperature hydrogen-gas sensing. *Int. J. Hydrogen Energy* **2016**, *41*, 5396–5404. [\[CrossRef\]](#)
71. Hong, J.; Lee, S.; Seo, J.; Pyo, S.; Kim, J.; Lee, T. A Highly Sensitive Hydrogen Sensor with Gas Selectivity Using a PMMA Membrane-Coated Pd Nanoparticle/Single-Layer Graphene Hybrid. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3554–3561. [\[CrossRef\]](#)
72. Alfano, B.; Polichetti, T.; Miglietta, M.L.; Massera, E.; Schiattarella, C.; Ricciardella, F.; Di Francia, G. Fully eco-friendly H₂ sensing device based on Pd-decorated graphene. *Sens. Actuators B Chem.* **2017**, *239*, 1144–1152. [\[CrossRef\]](#)
73. Chu, B.H.; Lo, C.; Nicolosi, J.; Chang, C.; Chen, V.; Strupinski, W.; Pearton, S.J.; Ren, F. Hydrogen detection using platinum coated graphene grown on SiC. *Sens. Actuators B Chem.* **2011**, *157*, 500–503. [\[CrossRef\]](#)
74. Vedala, H.; Sorescu, D.C.; Kotchey, G.P.; Star, A. Chemical Sensitivity of Graphene Edges Decorated with Metal Nanoparticles. *Nano Lett.* **2011**, *11*, 2342–2347. [\[CrossRef\]](#)
75. Shafiei, M.; Spizzirri, P.G.; Arsat, R.; Yu, J.; Du Plessis, J.; Dubin, S.; Kaner, R.B.; Kalantar-Zadeh, K.; Wlodarski, W. Platinum/Graphene Nanosheet/SiC Contacts and Their Application for Hydrogen Gas Sensing. *J. Phys. Chem. C* **2010**, *114*, 13796–13801. [\[CrossRef\]](#)
76. Shafiei, M.; Arsat, R.; Yu, J.; Kalantar-Zadeh, K.; Wlodarski, W.; Dubin, S.; Kaner, R. Pt/graphene nano-sheet based hydrogen gas sensor. In Proceedings of the SENSORS, 2009 IEEE, Christchurch, New Zealand, 25–28 October 2009; pp. 295–298.
77. Chu, B.H.; Nicolosi, J.; Lo, C.F.; Strupinski, W.; Pearton, S.J.; Ren, F. Effect of Coated Platinum Thickness on Hydrogen Detection Sensitivity of Graphene-Based Sensors. *Electrochem. Solid-State Lett.* **2011**, *14*, K43–K45. [\[CrossRef\]](#)
78. Kaniyoor, A.; Jafri, R.I.; Arockiadoss, T.; Ramaprabhu, S. Nanostructured Pt decorated graphene and multi walled carbon nanotube based room temperature hydrogen gas sensor. *Nanoscale* **2009**, *1*, 382. [\[CrossRef\]](#)
79. Harley-Trochimczyk, A.; Chang, J.; Zhou, Q.; Dong, J.; Pham, T.; Worsley, M.A.; Maboudian, R.; Zettl, A.; Mickelson, W. Catalytic hydrogen sensing using microheated platinum nanoparticle-loaded graphene aerogel. *Sens. Actuators B Chem.* **2015**, *206*, 399–406. [\[CrossRef\]](#)
80. Lu, X.; Song, X.; Gu, C.; Ren, H.; Sun, Y.; Huang, J. Freeze drying-assisted synthesis of Pt@reduced graphene oxide nanocomposites as excellent hydrogen sensor. *J. Phys. Chem. Solids* **2018**, *116*, 324–330. [\[CrossRef\]](#)
81. Zhu, L.; Jia, Y.; Gai, G.; Ji, X.; Luo, J.; Yao, Y. Ambipolarity of large-area Pt-functionalized graphene observed in H₂ sensing. *Sens. Actuators B Chem.* **2014**, *190*, 134–140. [\[CrossRef\]](#)
82. Yu, J.; Shafiei, M.; Ou, J.Z.; Shin, K.; Wlodarski, W. A study of hydrogen gas sensing performance of Pt/Graphene/GaN devices. In Proceedings of the 2011 IEEE SENSORS, Limerick, Ireland, 28–31 October 2011; pp. 1017–1020.
83. Pak, Y.; Kim, S.-M.; Jeong, H.; Kang, C.G.; Park, J.S.; Song, H.; Lee, R.; Myoung, N.; Lee, B.H.; Seo, S.; et al. Palladium-Decorated Hydrogen-Gas Sensors Using Periodically Aligned Graphene Nanoribbons. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13293–13298. [\[CrossRef\]](#) [\[PubMed\]](#)

84. Lange, U.; Hirsch, T.; Mirsky, V.M.; Wolfbeis, O.S. Hydrogen sensor based on a grapheme—Palladium nanocomposite. *Electrochim. Acta* **2011**, *56*, 3707–3712. [\[CrossRef\]](#)
85. Johnson, J.L.; Behnam, A.; Pearton, S.J.; Ural, A. Hydrogen Sensing Using Pd-Functionalized Multi-Layer Graphene Nanoribbon Networks. *Adv. Mater.* **2010**, *22*, 4877–4880. [\[CrossRef\]](#)
86. Chung, M.G.; Kim, D.-H.; Seo, D.K.; Kim, T.; Im, H.U.; Lee, H.M.; Yoo, J.B.; Hong, S.-H.; Kang, T.J.; Kim, Y.H. Flexible hydrogen sensors using graphene with palladium nanoparticle decoration. *Sens. Actuators B Chem.* **2012**, *169*, 387–392. [\[CrossRef\]](#)
87. Lee, J.S.; Oh, J.; Jun, J.; Jang, J. Wireless Hydrogen Smart Sensor Based on Pt/Graphene-Immobilized Radio-Frequency Identification Tag. *ACS Nano* **2015**, *9*, 7783–7790. [\[CrossRef\]](#)
88. Wu, W.; Liu, Z.; Jauregui, L.A.; Yu, Q.; Pillai, R.; Cao, H.; Bao, J.; Chen, Y.P.; Pei, S.-S. Wafer-scale synthesis of graphene by chemical vapor deposition and its application in hydrogen sensing. *Sens. Actuators B Chem.* **2010**, *150*, 296–300. [\[CrossRef\]](#)
89. Pandey, P.; Wilson, N.R.; Covington, J.A. Pd-doped reduced graphene oxide sensing films for H₂ detection. *Sens. Actuators B Chem.* **2013**, *183*, 478–487. [\[CrossRef\]](#)
90. Tang, X.; Haddad, P.-A.; Mager, N.; Geng, X.; Reckinger, N.; Hermans, S.; Debligny, M.; Raskin, J.-P. Chemically deposited palladium nanoparticles on graphene for hydrogen sensor applications. *Sci. Rep.* **2019**, *9*, 3653. [\[CrossRef\]](#) [\[PubMed\]](#)
91. Phan, D.-T.; Chung, G.-S. Characteristics of resistivity-type hydrogen sensing based on palladium-graphene nanocomposites. *Int. J. Hydrogen Energy* **2014**, *39*, 620–629. [\[CrossRef\]](#)
92. Phan, D.-T.; Chung, G.-S. A novel Pd nanocube–graphene hybrid for hydrogen detection. *Sens. Actuators B Chem.* **2014**, *199*, 354–360. [\[CrossRef\]](#)
93. Phan, D.-T.; Chung, G.-S. Reliability of hydrogen sensing based on bimetallic Ni–Pd/graphene composites. *Int. J. Hydrogen Energy* **2014**, *39*, 20294–20304. [\[CrossRef\]](#)
94. Sharma, B.; Kim, J.-S. Graphene decorated Pd–Ag nanoparticles for H₂ sensing. *Int. J. Hydrogen Energy* **2018**, *43*, 11397–11402. [\[CrossRef\]](#)
95. Huang, L.; Zhang, Z.; Li, Z.; Chen, B.; Ma, X.; Dong, L.; Peng, L.-M. Multifunctional Graphene Sensors for Magnetic and Hydrogen Detection. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9581–9588. [\[CrossRef\]](#)
96. Sun, Y.; Zhang, D.; Chang, H.; Zhang, Y. Fabrication of palladium–zinc oxide–reduced graphene oxide hybrid for hydrogen gas detection at low working temperature. *J. Mater. Sci. Mater. Electron.* **2016**, *28*, 1667–1673. [\[CrossRef\]](#)
97. Kaur, J.; Anand, K.; Kohli, N.; Kaur, A.; Singh, R.C. Temperature dependent selective detection of hydrogen and acetone using Pd doped WO₃/reduced graphene oxide nanocomposite. *Chem. Phys. Lett.* **2018**, *701*, 115–125. [\[CrossRef\]](#)
98. Du, Y.; Xue, Q.; Zhang, Z.; Xia, F. Great enhancement in H₂ response using graphene-based Schottky junction. *Mater. Lett.* **2014**, *135*, 151–153. [\[CrossRef\]](#)
99. Shiraz, H.G. Efficient room temperature hydrogen gas sensing based on graphene oxide and decorated porous silicon. *Int. J. Hydrogen Energy* **2017**, *42*, 15966–15972. [\[CrossRef\]](#)
100. Jin, L.; Zhou, Y.; Bai, X.; Chen, K.; Guan, B.-O. High-sensitivity and fast-response fiber-tip Fabry–Pérot hydrogen sensor with suspended palladium-decorated graphene. *Nanoscale* **2019**, *11*, 15821–15827. [\[CrossRef\]](#)
101. Shin, N.H.; Lee, J.S.; Jun, J.; An, J.H.; Kim, S.G.; Cho, K.H.; Jang, J. Flower-like Palladium Nanoclusters Decorated Graphene Electrodes for Ultrasensitive and Flexible Hydrogen Gas Sensing. *Sci. Rep.* **2015**, *5*, 12294. [\[CrossRef\]](#) [\[PubMed\]](#)
102. Kumar, R.; Varandani, D.; Mehta, B.R.; Singh, V.; Wen, Z.; Feng, X.; Müllen, K. Fast response and recovery of hydrogen sensing in Pd–Pt nanoparticle–graphene composite layers. *Nanotechnology* **2011**, *22*, 275719. [\[CrossRef\]](#) [\[PubMed\]](#)
103. Mondal, B.; Basumatari, B.; Das, J.; Roychaudhury, C.; Saha, H.; Mukherjee, N. ZnO–SnO₂ based composite type gas sensor for selective hydrogen sensing. *Sens. Actuators B Chem.* **2014**, *194*, 389–396. [\[CrossRef\]](#)
104. Ha, Y.; Jung, H.; Lee, Y.; Kim, M.H.; Lee, Y. Alteration of the morphology and electrocatalytic activity of IrO₂ nanowires upon reduction by hydrogen gas. *Sens. Actuators B Chem.* **2015**, *216*, 159–164. [\[CrossRef\]](#)
105. Huang, H.; Gong, H.; Chow, C.L.; Guo, J.; White, T.J.; Tse, M.S.; Tan, O.K. Low-Temperature Growth of SnO₂ Nanorod Arrays and Tunable n–p–n Sensing Response of a ZnO/SnO₂ Heterojunction for Exclusive Hydrogen Sensors. *Adv. Funct. Mater.* **2011**, *21*, 2680–2686. [\[CrossRef\]](#)

106. Ibrahim, I.M.; Hathal, Y.R.; Ibrahim, F.T.; ALI, M.H. Etching effect on sensing behavior of CuO: NiO/PS Hydrogen gas sensor. *Int. J. Sci. Eng. Res.* **2015**, *6*, 1664–1668.
107. Hu, J.; Sun, Y.; Xue, Y.; Zhang, M.; Li, P.; Lian, K.; Zhuikov, S.; Zhang, W.; Chen, Y. Highly sensitive and ultra-fast gas sensor based on CeO₂-loaded In₂O₃ hollow spheres for ppb-level hydrogen detection. *Sens. Actuators B Chem.* **2018**, *257*, 124–135. [[CrossRef](#)]
108. Motaung, D.E.; Mhlongo, G.; Makgwane, P.R.; Dhonge, B.; Cummings, F.R.; Swart, H.C.; Ray, S.S. Ultra-high sensitive and selective H₂ gas sensor manifested by interface of n–n heterostructure of CeO₂-SnO₂ nanoparticles. *Sens. Actuators B Chem.* **2018**, *254*, 984–995. [[CrossRef](#)]
109. Joy, N.A.; Nandasiri, M.I.; Rogers, P.; Jiang, W.; Varga, T.; Kuchibhatla, S.V.N.T.; Thevuthasan, S.; Carpenter, M.A. Selective Plasmonic Gas Sensing: H₂, NO₂, and CO Spectral Discrimination by a Single Au-CeO₂ Nanocomposite Film. *Anal. Chem.* **2012**, *84*, 5025–5034. [[CrossRef](#)]
110. Wan, Q.; Li, Q.H.; Chen, Y.J.; Wang, T.; He, X.L.; Li, J.P.; Lin, C.L. Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors. *Appl. Phys. Lett.* **2004**, *84*, 3654–3656. [[CrossRef](#)]
111. Yang, M.; Kim, D.-H.; Kim, W.-S.; Kang, T.J.; Lee, B.Y.; Hong, S.; Kim, Y.H.; Hong, S.-H. H₂ sensing characteristics of SnO₂ coated single wall carbon nanotube network sensors. *Nanotechnology* **2010**, *21*, 215501. [[CrossRef](#)]
112. Ratina, K.; Yang, W.; Ringer, S.; Braet, F. Toward Ubiquitous Environmental Gas Sensors—Capitalizing on the Promise of Graphene. *Environ. Sci. Technol.* **2010**, *44*, 1167–1176. [[CrossRef](#)] [[PubMed](#)]
113. Sundaram, R.S.; Balasubramanian, K.; Burghard, M.; Kern, K.; Gómez-Navarro, C. Electrochemical Modification of Graphene. *Adv. Mater.* **2008**, *20*, 3050–3053. [[CrossRef](#)]
114. Lu, G.; Park, S.; Yu, K.; Ruoff, R.S.; Ocola, L.E.; Rosenmann, D.; Chen, J. Toward Practical Gas Sensing with Highly Reduced Graphene Oxide: A New Signal Processing Method To Circumvent Run-to-Run and Device-to-Device Variations. *ACS Nano* **2011**, *5*, 1154–1164. [[CrossRef](#)] [[PubMed](#)]
115. Zhang, Y.; Zou, X.; Xu, L.; Liao, L.; Liu, W.; Ho, J.C.; Xiao, X.; Jiang, C.; Li, J. Hydrogen gas sensor based on metal oxide nanoparticles decorated graphene transistor. *Nanoscale* **2015**, *7*, 10078–10084. [[CrossRef](#)]
116. Munasinghe, M.A.H.M.; Comini, E.; Zappa, D.; Poli, N.; Sberveglieri, G. Low Temperature Gas Sensing Properties of Graphene Oxide/SnO₂ Nanowires Composite for H₂. *Procedia Eng.* **2016**, *168*, 305–308. [[CrossRef](#)]
117. Russo, P.A.; Donato, N.; Leonardi, S.G.; Baek, S.; Conte, D.E.; Neri, G.; Pinna, N. Room-Temperature Hydrogen Sensing with Heteronanostructures Based on Reduced Graphene Oxide and Tin Oxide. *Angew. Chem. Int. Ed.* **2012**, *51*, 11053–11057. [[CrossRef](#)]
118. Zhang, M.; Zhen, Y.; Sun, F.; Xu, C. Hydrothermally synthesized SnO₂-graphene composites for H₂ sensing at low operating temperature. *Mater. Sci. Eng. B* **2016**, *209*, 37–44. [[CrossRef](#)]
119. Dhall, S.; Kumar, M.; Bhatnagar, M.; Mehta, B. Dual gas sensing properties of graphene-Pd/SnO₂ composites for H₂ and ethanol: Role of nanoparticles-graphene interface. *Int. J. Hydrogen Energy* **2018**, *43*, 17921–17927. [[CrossRef](#)]
120. Esfandiar, A.; Ghasemi, S.; Irajizad, A.; Akhavan, O.; Gholami, M. The decoration of TiO₂/reduced graphene oxide by Pd and Pt nanoparticles for hydrogen gas sensing. *Int. J. Hydrogen Energy* **2012**, *37*, 15423–15432. [[CrossRef](#)]
121. Esfandiar, A.; Irajizad, A.; Akhavan, O.; Ghasemi, S.; Gholami, M.R. Pd-WO₃/reduced graphene oxide hierarchical nanostructures as efficient hydrogen gas sensors. *Int. J. Hydrogen Energy* **2014**, *39*, 8169–8179. [[CrossRef](#)]
122. Chen, M.; Zou, L.; Zhang, Z.; Shen, J.; Li, D.; Zong, Q.; Gao, G.; Wu, G.; Zhang, Z. Tandem gasochromic-Pd-WO₃/graphene/Si device for room-temperature high-performance optoelectronic hydrogen sensors. *Carbon* **2018**, *130*, 281–287. [[CrossRef](#)]
123. Na, C.W.; Woo, H.-S.; Kim, I.-D.; Lee, J.-H. Selective detection of NO₂ and C₂H₅OH using a Co₃O₄-decorated ZnO nanowire network sensor. *Chem. Commun.* **2011**, *47*, 5148. [[CrossRef](#)]
124. Abideen, Z.U.; Kim, H.W.; Kim, S.S. An ultra-sensitive hydrogen gas sensor using reduced graphene oxide-loaded ZnO nanofibers. *Chem. Commun.* **2015**, *51*, 15418–15421. [[CrossRef](#)]
125. Singh, G.; Choudhary, A.; Haranath, D.; Joshi, A.G.; Singh, N.; Singh, S.; Pasricha, R. ZnO decorated luminescent graphene as a potential gas sensor at room temperature. *Carbon* **2012**, *50*, 385–394. [[CrossRef](#)]
126. Anand, K.; Singh, R.C.; Singh, M.P.; Kaur, J.; Singh, R.C. Hydrogen sensor based on graphene/ZnO nanocomposite. *Sens. Actuators B Chem.* **2014**, *195*, 409–415. [[CrossRef](#)]

127. Tabares, G.; Redondo-Cubero, A.; Vazquez, L.; Revenga, M.; Cortijo-Campos, S.; Lorenzo, E.; De Andrés, A.; Ruiz, E.; Pau, J. A route to detect H₂ in ambient conditions using a sensor based on reduced graphene oxide. *Sens. Actuators A Phys.* **2020**, *304*, 111884. [[CrossRef](#)]
128. Drmosh, Q.; Hendi, A.; Hossain, M.; Yamani, Z.H.; Moqbel, R.; Hezam, A.; Gondal, M. UV-activated gold decorated rGO/ZnO heterostructured nanocomposite sensor for efficient room temperature H₂ detection. *Sens. Actuators B Chem.* **2019**, *290*, 666–675. [[CrossRef](#)]
129. Liu, J.W.; Wu, J.; Ahmad, M.Z.; Wlodarski, W. Hybrid aligned zinc oxide nanowires array on CVD graphene for hydrogen sensing. In Proceedings of the 2013 Transducers & Eurosensors XXVII: The 17th International Conference on Solid-State Sensors, Actuators and Microsystems (TRANSDUCERS & EUROSENSORS XXVII), Barcelona, Spain, 16–20 June 2013; pp. 194–197.
130. Chen, H.; Tsai, H.J.; Lin, T.C.; Weng, W.C.; Chang, Y.C.; Chiu, J.L.; Lin, J.J.; Lin, C.-F.; Lin, Y.S.; Chen, H. Incorporation of carbon nanotube and graphene in ZnO nanorods-based hydrogen gas sensor. *Ceram. Int.* **2018**, *44*, 12308–12314. [[CrossRef](#)]
131. Dutta, D.; Hazra, S.; Das, J.; Sarkar, C.; Basu, S. Studies on p-TiO₂/n-graphene heterojunction for hydrogen detection. *Sens. Actuators B Chem.* **2015**, *212*, 84–92. [[CrossRef](#)]
132. Kamal, T. High performance NiO decorated graphene as a potential H₂ gas sensor. *J. Alloy. Compd.* **2017**, *729*, 1058–1063. [[CrossRef](#)]
133. Zhang, D.; Yin, N.; Jiang, C.; Xia, B. Characterization of CuO–reduced graphene oxide sandwiched nanostructure and its hydrogen sensing characteristics. *J. Mater. Sci. Mater. Electron.* **2016**, *28*, 2763–2768. [[CrossRef](#)]
134. Arsat, R.; Breedon, M.; Shafiei, M.; Spizziri, P.; Gilje, S.; Kaner, R.; Kalantar-Zadeh, K.; Wlodarski, W. Graphene-like nano-sheets for surface acoustic wave gas sensor applications. *Chem. Phys. Lett.* **2009**, *467*, 344–347. [[CrossRef](#)]
135. Achary, L.S.K.; Maji, B.; Kumar, A.; Ghosh, S.P.; Kar, J.P.; Dash, P. Efficient room temperature detection of H₂ gas by novel ZnFe₂O₄–Pd decorated rGO nanocomposite. *Int. J. Hydrogen Energy* **2020**, *45*, 5073–5085. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).