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Nanostructured Platinum and Platinum Alloy-Based Resistive Hydrogen Sensors: A Review †

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Abstract: As a future energy source, hydrogen is used in many industrial applications, such as chemicals, semiconductors, transportation, etc. Hydrogen gas, which has many unusual properties compared to other gases, has the risk of being flammable and explosive when it is present in the atmosphere at concentrations of 4% and higher. We need hydrogen sensors both to determine the risks in advance and because we do not want hydrogen gas, which is a source of energy, to be lost due to leakage. Hydrogen sensors are used in hydrogen production plants to determine hydrogen purity, for leakage and safety in all areas where hydrogen gas is used, and also in the medical field, as hydrogen gas is a marker in disease diagnosis. In the context of classifying hydrogen sensors according to their physicochemical sensing mechanisms, resistive metallic hydrogen sensors stand out as a prevalent choice, with Pd, Pt, and their alloy counterparts being commonly employed as designated sensing materials. In this study, nanostructured platinum (Pt) and Pt alloy-based resistive hydrogen sensors are reviewed and discussed in detail. The sensing mechanism of Pt-based resistive hydrogen sensors has been explained by the scattering of charge carriers at the surface, coupled with its defects and grain boundaries, and by the formation of hydride (PtH_x) phenomena, depending on the increase or decrease in resistance in the hydrogen environment.

Keywords: platinum; alloy; thin film; nanowire; nanoporous; hydrogen sensor; resistive sensor

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1. Introduction

Hydrogen, a naturally abundant renewable energy source, holds remarkable potential as an efficient and environmentally clean option. It finds diverse industrial applications across sectors such as chemistry, where it serves as a crucial reducing agent in crude oil refining, plastics production, and the flat glass industry. Additionally, its utility extends to food product processing through oil and fat hydrogenation, semiconductor fabrication as a process gas for thin-film deposition and annealing atmospheres, and even transportation applications involving fuel cells and spacecrafts [1].

However, it is a gas with a low ignition energy of hydrogen and a lower explosion limit of 4% in air. Therefore, a slight gas leak can cause serious concern and the use of hydrogen poses a serious safety concern. Since hydrogen gas is colorless, odorless, tasteless, and cannot be detected by the human senses, safety is an important parameter when working with hydrogen-containing gases [1]. Given these imperatives, the development of hydrogen sensors assumes a pivotal role. Rapid responsiveness, an extensive sensing range, and the capacity for integration into large-scale urban networks stand as prerequisites. Furthermore, ongoing research endeavors aim to refine the sensitivity, selectivity, response time, and overall reliability of these sensors. Simultaneously, concerted efforts are directed towards minimizing sensor dimensions, reducing costs, and optimizing power consumption, aligning with the prospective surge in hydrogen's technological applications [2].

Hydrogen gas sensors are purposefully designed devices intended to monitor, detect, and measure the presence and concentration of hydrogen gas within a designated area using various methods. In light of the discernible physicochemical principles governing their detection mechanisms, hydrogen sensors have undergone comprehensive studies and can be systematically categorized into nine well-defined groups. These classifications encompass resistive sensors (semiconducting metal–oxide and metallic resistors), work function-based, catalytic, electrochemical, optical, thermal conductivity, mechanical, acoustic, and magnetic [2,3]. Notably, within this diverse range, resistive metallic hydrogen sensors have consistently showcased exceptional performance, securing a coveted position at the forefront of these categories [2]. In the realm of metallic resistive hydrogen sensors, it is commonplace to utilize Pd, Pt, and their corresponding alloys as primary sensing materials [4,5]. The hydrogen sensing properties of Pt, Pt alloys, and Pt layered structures in many nanostructures such as nanowires, nanoporous materials, and thin films have been investigated [6–12]. This study aims to comprehensively analyze various Pt nanostructures and Pt-based alloy resistive hydrogen sensors, delving into their performance and sensing mechanisms. By conducting an in-depth exploration through an extensive literature review, the goal is to enhance our understanding of hydrogen sensing technologies, potentially influencing their future applications and development.

2. Sensing Mechanism of Pt-Based Resistive Hydrogen Sensors

Fundamentally, the sensing mechanism of Pt-based resistive hydrogen sensors could be examined with two mechanisms, depending on the increase or decrease in the resistance of the sensor during exposure to hydrogen. The decrease in the resistance of Pt nanostructures during hydrogen exposure is generally explained by the surface scattering phenomenon [6,8,9,13,14]. At normal atmospheric conditions, the surface of Pt nanostructures is covered with absorbed oxygen atoms. During exposure to hydrogen, the hydrogen atoms are replaced with oxygen atoms at the Pt surface and the number of charge carriers scattering on the surface decreases; as a consequence, the resistance of Pt nanostructures decreases.

The phenomenon of enhanced resistance observed in Pt nanostructures in hydrogen-rich environments can be explained by three distinct mechanisms. Firstly, the increase in Pt resistance resulting from hydrogen exposure can be traced back to the formation of PtHx hydride [7]. Notably, it has been confirmed that the presence of oxygen in the surrounding environment does not exert any noticeable influence on the hydrogen sensing capabilities of resistive Pt sensors [7]. Secondly, the observed elevation in Pt resistance within the hydrogen environment can be attributed to electron scattering phenomena arising from inherent defects within the Pt nanostructure [10]. Lastly, the escalation in Pt resistance experienced in the hydrogen environment can also be associated with electron scattering occurring at the grain boundaries of Pt nanoparticles [15].

3. Discussion

A comprehensive literature review of hydrogen gas sensor performance using Pt and Pt-based alloys is presented in Table 1. This review focuses on variations in thickness, chemical compositions, and structural configurations, presenting a comprehensive exploration of the intricate interplay between these elements and the resulting sensing capabilities. These materials encompass an assortment of formats, ranging from standalone Pt nanowires to intricately designed Pt nanowire arrays. The sensitivities exhibited by these materials span an intriguing range, extending from approximately 3.5% to an impressive 18.4%, a variance inherently tied to the intricate dynamics of concentration and temperature modulation. Additionally, the influence of alloying and hybridization emerges as a significant factor in the observed sensitivities, becoming particularly evident in the cases of Pt-modified

Pd nanowires and core–shell nanocrystal layers, where sensitivities converge around the 4% range, potentially enhanced by temperature effects. A closer look at Pt-based thin films reveals a wide variety of thicknesses, ranging from 2 nm to 150 nm. These films, embodying differing thicknesses, have been meticulously tailored to respond optimally to distinct hydrogen concentration ranges and temperature conditions. As the table elucidates, the range of sensitivities for these films encompasses values as varied as 0.4% to an astonishing 261%. This span underscores the criticality of film thickness and operating parameters in determining the efficiency of these sensors. Noteworthy variations in performance are showcased in nanoporous Pt films and bimetallic Pt/Pd films, revealing elevated sensitivities of approximately 13.5% and 13.0%, respectively. Further enriching the diversity of Pt-based materials are Pt alloys, such as Pt75Co25 and Pt79Ni21, which contribute valuable insights into the influence of alloy composition on sensitivity performance. Displaying sensitivities ranging from 1.25% to 2.6%, these alloys highlight the intricate relationship between material composition and the consequent sensor response. Ultimately, the table shows the complexities of Pt-based hydrogen sensing materials' behavior with respect to concentration ranges and temperatures. This compilation underscores the crucial role played by material design, composition, and environmental factors in shaping the efficacy and potential applications of these sensors, providing a nuanced perspective that contributes to the continual evolution of advanced hydrogen sensing technologies.

Table 1. Conducting a literature review to compare hydrogen gas sensitivities across different Pt-based material types, their corresponding structural forms, and different operating temperatures.

Materials	H_2 Concentration Range (ppm)	Temperature (°C)	Sensitivity (S%)	Ref
Pt nanowire	1000–50,000	RT—277	~3.5 (275 °C for 10,000 ppm)	[8]
Pt nanowire array	1–1,000,000	200	~18.4 (for 10,000 ppm)	[10]
Pt nanowire array	1–1000	RT	~5 (RT for 1000 ppm)	[14]
Pt-modified Pd nanowires	500–50,000	RT to 100	~4 (RT for 10,000 ppm)	[16]
Pd@Pt core–shell nanocrystal layer	10–40,000	RT to 250	~3.6 (150 °C for 10,000 ppm)	[17]
Pt@Au core–shell nanoparticle layer	1000–100,000	RT to 80	~15 (RT for 100,000 ppm)	[15]
PtOx/Pt nanowire	0.5–1000	RT	~65 (for 500 ppm)	[18]
Ultrafine Pt nanowire network	1–5000	RT	~261 (for 5000 ppm)	[19]
3.5 nm Pt thin film	10–1000	RT	1 (for all conc.)	[6]
		100	~4 (for 500 ppm)	
		200	~8 (for 500 ppm)	
10 nm Pt thin film	10–10,000	RT to 60	~1.5 (RT for 10,000 ppm)	[20]
20 nm Pt thin film			~0.5 (RT for 10,000 ppm)	
40 nm Pt thin film			~0.4 (RT for 10,000 ppm)	
5 nm Pt thin film	100–10,000	RT	~4 (for 10,000 ppm)	[21]
2 nm Pt thin film	1000–10,000	RT to 200	~2.8 (RT for 1000 ppm)	[9]
5 nm Pt thin film	0.5–200	150	~4.5 (for 200 ppm)	[13]
2 nm Pt thin film	30–1000	RT to 100	~2.4 (RT for 1000 ppm)	[22]
150 nm Pt nanoporous film	100–1000	RT to 100	3.5 (RT for 1000 ppm)	[7]
3 nm Nanoporous Pt Film	10–50,000	RT to 150	13.0 (RT for 10,000 ppm)	[12]
Pt/Pd bimetallic film	10–40,000	RT to 150	13.5 (150 °C for 10,000 ppm)	[23]

Table 1. *Cont.*

Materials	H_2 Concentration Range (ppm)	Temperature (°C)	Sensitivity (S%)	Ref
2 nm Pt75Co25 alloy thin film	10–50,000	RT to 150	1.25 (150 °C for 10,000 ppm)	[24]
2 nm Pt79Ni21 alloy thin film	25–1000	RT to 200	~2.6 (RT for 1000 ppm)	[11]

4. Conslusions

As a conclusion, this review paper delves into the intricate realm of Pt-based hydrogen gas sensors, shedding light on their intrinsic potential and highlighting the pivotal role of various structural attributes. The profound importance of these attributes, including ultrathin films, nanopores, nanowires, and core–shell configurations, in shaping hydrogen gas sensitivity has been thoroughly expounded. Throughout this exposition, it becomes resoundingly clear that the Pt structures' surfaces stand as a fundamental and non-negotiable determinant of sensing performance, unveiling a key dimension for future explorations.

In a review that synthesizes existing knowledge, it is evident that purposeful modifications to Pt surfaces serve as a beacon of promise, offering a pathway for substantial enhancement in sensor efficacy. Beyond surface modifications, the intricate manipulation of nanostructure dimensions has exhibited the dual capability of heightening sensitivity while significantly refining response and recovery times. Moreover, the strategic introduction of surface defects within Pt nanostructures emerges as a judicious strategy, augmenting sensitivity levels and subsequently elevating the overall sensing performance.

As this review journeys through the expansive landscape of Pt-based hydrogen gas sensors, it also foresees a panorama of possibilities for future advancement. The envisioned innovative avenues encompass the discerning formulation of Pt alloys, incorporating diverse metallic constituents, as well as the intricate realization of layered structural motifs. Furthermore, the orchestrated engineering of intricate core–shell architectures and hybridized structures hold promise for advancing hydrogen gas sensors to new horizons. Collectively, the nuanced strategies unearthed within the breadth of this review underscore the rich potential for propelling Pt-based hydrogen gas sensors into a realm of heightened sensitivity and extended utility, thereby shaping the future landscape of sensing technologies.

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