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Effect of Noble Metals on Hydrogen Sensing Properties of Metal Oxide-based Gas Sensors

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Abstract

As a green and abundant source of energy, H2 has attracted the attention of researchers for use in different applications. Nevertheless, it is highly flammable, and because of its significantly small size, extreme attention is needed to detect its leakage. In this review, we discuss different effects of noble metals on the H2 gas response and performance of metal oxide-based gas sensors. In this regard, we discuss the effects of noble metals, in combination with metal oxides, on H2 gas detection. The catalytic activity towards H2 gas and the formation of heterojunctions with metal oxides are the main contributions of noble metals to the sensing improvement of H2 gas sensors. Furthermore, in the special case of Pd and somewhat Pt, the formation of PdHx and PtHx also affects the H2 sensing performance. This review paper provides useful information for researchers working in the field of H2 gas detection.

Keywords: Noble metal, Metal oxide, Gas sensor

1. Hydrogen Gas and hydrogen Gas sensors

H_2 constitutes ~75% of the mass of the universe, and upon combustion, it only produces H_2O [1]. Thus, it is regarded as a clean, abundant, and renewable energy source [2]. It is used in hydrogen batteries [3], fuel cells [4], etc. [5]. However, it is a highly explosive gas due to low ignition temperature (520-580°C) and energy (~0.017 mJ), large flame propagation energy, high heat of combustion (286 kJ/mol), and wide air flammable range (4–74%) [6,7]. Moreover, at high concentrations, hydrogen will hinder an adequate supply of oxygen, causing asphyxiation [8]. Owing to such features, along with no color, odor, and taste [9], rapid and accurate detection of hydrogen is of importance in various fields. In this context, different hydrogen gas sensors such as electrochemical [10], catalytic combustion [11], thermoelectric [12], optical [13], gasochromic [14, 15], colorimetric [16], Pd-film and Pd-alloy films [17], and metal oxide-based [18], have been developed. Among them, metal oxide gas sensors are highly popular because of their high sensitivity, high stability, fast response time, and low price [19,20]. However, the main disadvantage of metal oxide sensors is their poor selectivity. In this regard, different approaches, such as p-n junction formation [21] and noble metal decoration [22], have been used to enhance the selectivity toward a specific gas. Herein, we only focus on the decoration of noble metals to enhance the hydrogen gas sensing properties of metal oxides.

2. Noble Metal Decoration

Noble metals can be decorated on the surface of host sensing materials using various methods such as UV-reduction [23], gamma-ray irradiation [24], chemical reduction [25], and sputtering [26]. Regardless of the decoration method, generally two mechanisms, namely, chemical sensitization and electronic sensitization, are responsible for the enhancement of hydrogen gas sensing properties in the presence of noble metals [27,28]. Chemical sensitization mainly manifests as a catalytic effect [29]. In this type of sensitization, as shown in Fig. 1 (a), hydrogen molecules dissociate into hydrogen atoms on the surface of noble metal NPs, and then spill over (migrate) to the surface of the host material [30], thus accelerating the gas sensing reactions through subsequent reaction with the already adsorbed oxygen ions at the surface of the gas sensor [31,32]:

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$$H_2(g) \xrightarrow{Noble\ metal} 2H \quad (1)$$

Hydrogen atoms are transported to the metal oxide through diffusion and can access additional sites on the surface of the metal oxide sensing layer. Obviously, the creation of more intimate contacts between the noble metal NPs and the metal oxides can enhance the response of the gas sensor [33]. Zhu *et al.* reported that without Pt NPs, self-heated $W_{18}O_{49}$ gas sensors did not show any response to H_2 gas, demonstrating the promising catalytic role of Pt for H_2 gas [34]. Noble metals such as Pt and Pd are particularly active for oxidation reactions because the heat of adsorption of oxygen on noble metals is sufficiently low to allow relatively low activation energy of oxidation and consequently a rapid rate of reactions. Thus, it is expected that the optimal sensing temperature of noble metal-decorated hydrogen gas sensors is lower than that of pristine gas sensors [35].

Electronic sensitization occurs through a direct electronic interaction between the noble metal NPs and the metal oxide surface (Fig. 1 (b)). When the oxidation state of the noble metal changes with the surrounding atmosphere, the electronic state of the metal oxide changes accordingly. More specifically, typical sensitizers of this type (Ag and Pd) are known to form stable oxides (Ag_xO and PdO_x) in air, while they are easily reduced to metals with a reducing gas. The observed work-function shifts indicate that each promoter in the oxidized form produces a strongly electron-depleted layer inside the metal oxide, while the electronic interaction is inhibited when it is reduced to metal. However, since Pt and Au generally cannot form stable oxides under these conditions, they do not show such sensitization [28].

As a hydrogen reactant, Pd has a particular affinity for hydrogen. Pd can uptake more than 600 times its own volume of hydrogen gas [36]. When hydrogen appears near Pd NPs, molecular H_2 dissociates into atomic H, which is characterized by a high dissociation rate. At low concentrations of H_2 gas, a solid solution of H_2 in the host metal (α-phase) is formed. With further increase of H_2, a new phase called β-phase starts forming, where both the α-phase and β-phase co-exist in equilibrium. A further increase in the H_2 concentration will result in the growth of the β-phase region at the expense of the α-phase. Finally, when the concentration of hydrogen reaches a certain value, the entire Pd is transformed into the β-phase (PdH_x), as shown in Fig. 2.

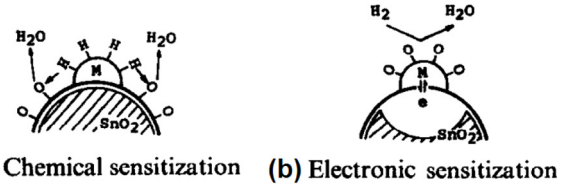

Fig. 1. (a) Chemical and (b) electronic sensitizations in noble metal decorated SnO_2 [28].

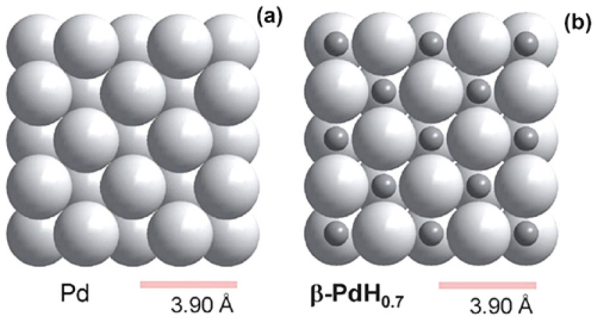

Fig. 2. (100) crystalline plane of (a) metallic Pd and (b) β-$PdH_{0.7}$ [37].

The overall reaction can be represented as follows [38, 39]:

$$(\alpha)Pd+x/2H_2 \leftrightarrow (\beta)PdH_x \quad (2)$$

Lee *et al.* [40] reported the hydrogen-sensing properties of Pd-decorated In_2O_3-ZnO nanofibers. As shown in Fig. 3, initially in air, Pd-ZnO Schottky barriers were formed; subsequently, in the presence of H_2 gas, the formation of PdH_x with a very different work function (3.7 eV) than Pd destroyed the Schottky barriers to form Ohmic contacts, which eventually resulted in a highly modulated sensor resistance.

It should be noted that the formation of PdH_x leads to changes in the physical properties of metallic Pd, including changes in volume and electrical resistivity. Therefore, pristine Pd thin films were also used for the detection of hydrogen gas [41,42]. Similarly, Pt can form PtH_x in the presence of hydrogen gas [43]. However, the degree of hydrogen adsorption is much lower than that of Pd.

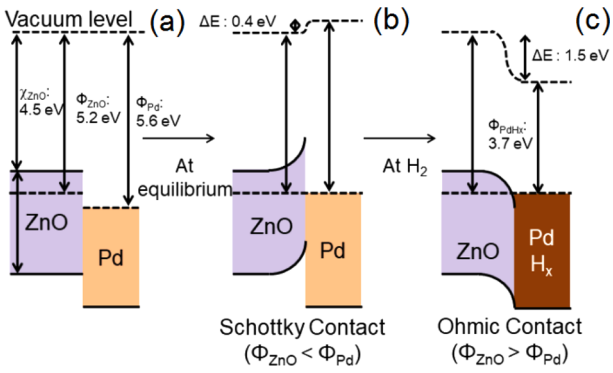

Fig. 3. (a) Energy levels of Pd and ZnO before contact and after contact in (a) air and (b) hydrogen atmosphere [40].

3. Conclusions

Noble metal decoration is a promising approach to enhance the hydrogen gas sensing properties of metal oxide gas sensors. Noble metal NPs well-dispersed on the surface of metal oxides can affect the response towards hydrogen gas primarily through chemical sensitization and electronic sensitization. Furthermore, Pd and Pt noble metals can adsorb hydrogen atoms, leading to significant changes in the work function upon exposure to hydrogen gas and subsequent electronic interactions with the host metal oxide, leading to an improvement in the response to hydrogen gas.

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