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Hydrogen Sensing of Graphene-based Chemoresistive Gas Sensor Enabled by Surface Decoration

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Abstract

Hydrogen (H_2) is considered as a new clean energy resource for replacing petroleum because it produces only H_2O after the combustion process. However, owing to its explosive nature, it is extremely important to detect H_2 gas in the ambient atmosphere. This has triggered the development of H_2 gas sensors. 2-dimensional (2D) graphene has emerged as one of the most promising candidates for chemical sensors in various industries. In particular, graphene exhibits outstanding potential in chemoresistive gas sensors for the detection of diverse harmful gases and the control of indoor air quality. Graphene-based chemoresistive gas sensors have attracted tremendous attention owing to their promising properties such as room temperature operation, effective gas adsorption, and high flexibility and transparency. Pristine graphene exhibits good sensitivity to NO_2 gas at room temperature and relatively low sensitivity to H_2 gas. Thus, research to control the selectivity of graphene gas sensors and improve the sensitivity to H_2 gas has been performed. Noble metal decoration and metal oxide decoration on the surface of graphene are the most favored approaches for effectively controlling the selectivity of graphene gas sensors. Herein, we introduce several strategies that enhance the sensitivity of graphene gas sensors to H_2 gas.

Keywords : Gas sensors, Graphene, Hydrogen sensing, Metal oxide decoration, Noble metal decoration

1. INTRODUCTION

Hydrogen (H_2) is one of the most abundant gas in ambient atmosphere. Moreover, H_2 only produces H_2O after the combustion process, which can be regarded as a clean energy source [1,2]. Hydrogen energy industries have gained tremendous attraction for replacing the petroleum [3,4]. However, H_2 is explosive, invisible, and odorless which requires an effective detection of H_2 molecules in ambient atmosphere [5,6]. The excess 4 vol% of H_2 concentration in ambient air becomes flammable which needs to be detected accurately. The real-time detection of H_2 gas was performed by various approaches such as gas chromatography, mass spectroscopy, thermal conductivity and chemoresistive gas sensor [7]. Among them, chemoresistive gas sensors are the most promising type thanks to simple fabrication process, low cost, and low electrical power consumption [8,9]. Basically, chemoresistive gas sensor detect the variation of electrical resistance in base air atmosphere and in target gas atmosphere. For decades, numerous materials were applied in chemoresistive gas sensor such as metal oxide, 2D materials and various hybrid composites. Metal oxides were the initially developed materials for chemoresistive gas sensors due to high response to target gas, rapid response, rapid recovery, and flexibility in fabrication of nanostructures [10,11]. However, the main drawback of metal oxide based chemoresistive gas sensor is that the operation is available at high temperature above 200°C [12]. To elevate the temperature, an external heating system is required which increases the electrical power consumption. This indicates that room temperature operation is significant to reduce the electrical power consumption.

2D materials have become excellent candidates to substitute the metal oxides. Among various 2D materials, graphene is the most representative material which is applied in diverse applications including electronics, optoelectronics and sensors thanks to high carrier mobility, high chemical stability, tunable band gap, high transparency, and flexibility [13-15]. The 2D planar carbon atoms possess large specific surface area which facilitates the gas adsorption at room temperature [16-19]. Thus, pristine graphene exhibit high response to NO_2 molecules at room temperature. Owing to the outstanding properties of graphene as a chemoresistive gas sensor, various approaches have been reported to detect H_2 gas by

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controlling the surface of graphene.

In this review, we introduce several approaches for effective detection of H_2 gas such as noble metal decoration and metal oxide decoration. The synthesis procedure, fabrication of the sensor devices and gas sensing properties of each strategies are explained. Moreover, the effect of decoration and surface modification of graphene on the selectivity will be further studied and compare the gas sensing characteristics of the reported graphene based H_2 gas sensors.)

2. GRAPHENE-BASED HYDROGEN GAS SENSORS

2.1 Metal oxide-decorated graphene hydrogen sensor

Films of metal oxides such as WO_3, TiO_2, ZnO, and SnO_2 have been widely used as sensing materials for hydrogen detection [20-22]. However, these metal oxide-based sensors require high operating temperatures for sufficient sensing performance. To overcome this limitation, various works have studied the combination of graphene materials with metal oxide nanoparticles [23,24]. Although pure graphene materials do not sensitively detect hydrogen gas, combining them with metal oxide nanoparticles enables highly sensitive and fast hydrogen sensing at room temperature. Zhang *et al.* investigated a room-temperature hydrogen sensor based on SnO_2-decorated graphene transistors [25]. They used the mechanical exfoliation method to prepare graphene and transferred the exfoliated graphene to a SiO_2/Si substrate. Tin oxide nanoparticles were formed by annealing the sample after metal film deposition. The device fabrication process was completed by the formation of electrodes using electron beam lithography and Cr/Au deposition. The prepared SnO_2 nanoparticle-decorated graphene gas sensors exhibited a fast response to hydrogen and short recovery times of less than 1 s at room temperature. The high sensitivity and fast response are explained by the small energy barrier between SnO_2 and graphene and the high carrier mobility of graphene. Kathiravan *et al.* reported the gas sensing properties of a self-assembled hierarchical ZnO nanotube/graphene-based sensor. The sensor exhibited high response and stability, and a fast reaction to hydrogen at room temperature [26]. The graphene was synthesized by the chemical vapor deposition (CVD) method and transferred to a SiO_2/Si substrate. Then, vertically aligned ZnO nanotubes were grown on the prepared graphene using the hydrothermal method. Finally, Pt interdigitated electrodes were fabricated on the hydrogen sensors. The sensors were prepared using various ZnO nanotube growth times. Fig. 1 shows the response curves of the sensors under 100 ppm hydrogen gas at room temperature and their responses to other gases. The sensing characteristics were altered depending on the growth condition and structural characteristics. In particular, the sensor based on defect-free ZnO nanotubes and graphene exhibited the largest response to hydrogen gas. The superb hydrogen sensing properties are attributed to the multiple depletion layers induced by the formation of metalized regions in the ZnO nanotube/graphene interfaces.

2.2 Noble metal-decorated graphene hydrogen sensor

Decoration with nanoparticles of noble metals such as Au, Ag, Pd, and Pt is a promising strategy for enhancing the sensitivity and

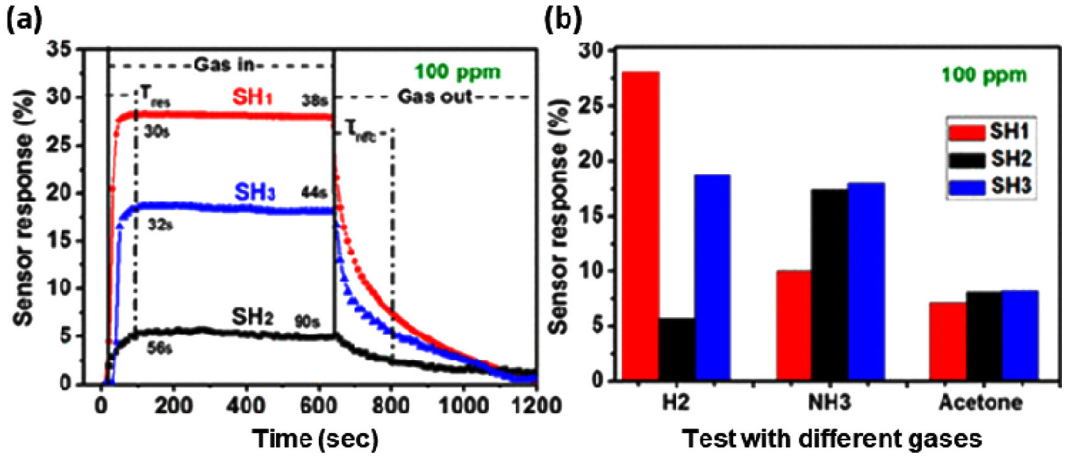

Fig. 1. (a) Response and recovery curves of the sensors with growth periods of 8 (red), 12 (blue), and 18 h (black line). (b) Response of each sensor to various gases. Reprinted with permission from [26]. Copyright © 2017, American Chemical Society.

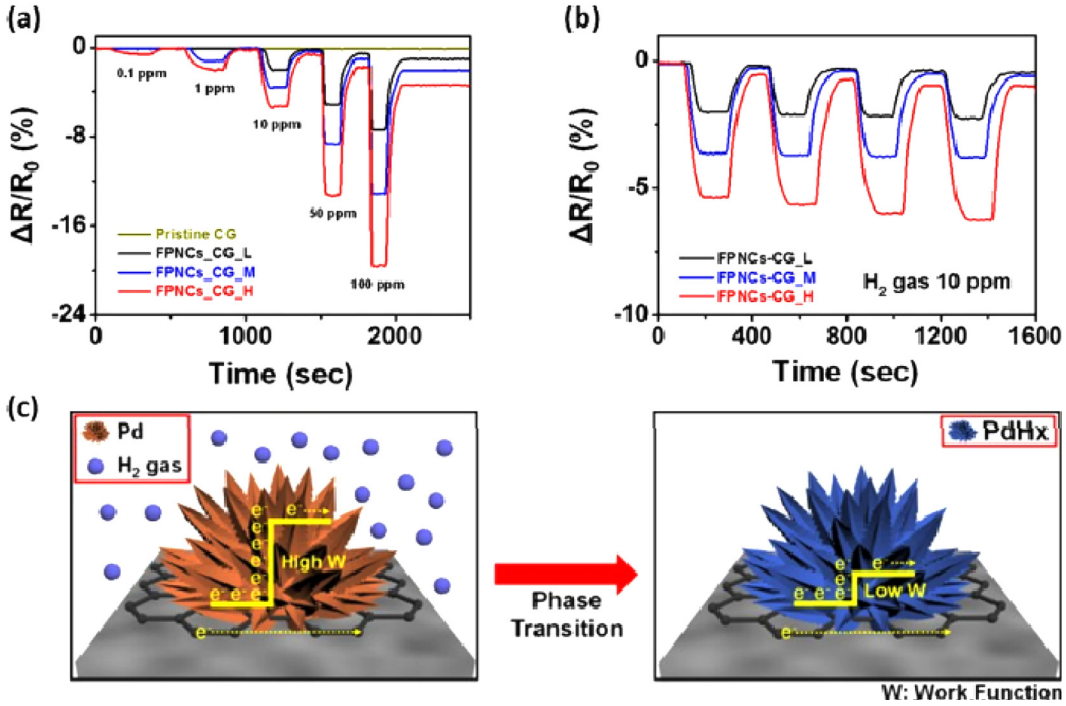

Fig. 2. Response curves at room temperature upon (a) exposure to various concentrations of hydrogen gas (0.1 to 100 ppm) and (b) periodic exposure to 10 ppm hydrogen gas of pristine graphene (green) and flower-like Pd nanocluster-decorated graphene with 0.01 (black), 0.1 (blue) and 1 M (red) 1,5-diaminonaphthalene. (c) Scheme of hydrogen gas sensing mechanism in flower-like Pd nanocluster- decorated graphene. Reprinted with permission from [35]. Copyright © 2015, Dong Hoon Shin *et al.*

selectivity of graphene-based gas sensors through functionalizing the surface chemistry [27,28]. The noble metal nanoparticles introduced on the graphene-based materials change the band gap and work function of graphene and induce carrier transfer. In addition, the noble metal nanoparticles modify the surface morphology and function as catalytic centers, resulting in variations of the sensing properties [29-31]. In particular, surface functionalization using Pt and Pd nanoparticles is a well-known method for enhancing the detection of hydrogen gas. The catalytic effect of the nanoparticles accelerates the dissociation of hydrogen molecules into more reactive atomic forms [32,33].

Kaniyoor *et al.* investigated room-temperature hydrogen gas sensors based on Pt-decorated graphene sheets and Pt-decorated multi-walled carbon nanotubes (MWCNTs) [34]. The graphene sheets were prepared by a thermal exfoliation method, and the MWCNTs were synthesized by a catalytic CVD method. Pt nanoparticle decoration was then achieved using chemical reduction from a Pt salt. The prepared samples were ultrasonically dispersed and drop-casted onto the electrodes to complete the sensor fabrication. The gas sensor based on the Pt-decorated graphene sheets showed a two-fold increase in the response compared to the sensor based on Pt-decorated MWCNTs. The sensing mechanism is the decrease in the work function due to hydrogen exposure. The lowered work function transfers electrons from the Pt nanoparticles to the graphene-based materials, which causes a decrease in the hole carriers and an increase in the sensor resistance. Because the graphene sheets contain more hole carriers than the carbon nanotubes, the recombination occurs at a increased rate in the Pt-decorated graphene-based sensor, resulting in a higher hydrogen sensitivity.

Shin *et al.* reported a method for fabricating flower-like Pd nanocluster-decorated graphene electrodes and the sensitive and reversible hydrogen sensing properties of these electrodes at room temperature [35]. First, CVD graphene was transferred to a poly(ethylene naphthalate) substrate and chemically functionalized by reacting with 1,5-diaminonaphthalene. Then, Pd nanoparticles were deposited directly on the graphene surface by electrodeposition. Flower-like palladium nanoclusters were formed as the deposition time increased. Fig. 2(a) shows the response curves of the electrodes with various functionalization solutions containing 0.01, 0.1, and 1 M 1,5-diaminonaphthalene under exposure to increasing hydrogen gas concentrations. The response increased with the number of flower-like palladium nanoclusters. This indicates that the palladium nanoclusters act as active materials for

reacting with hydrogen molecules (Fig. 2(b)). When the decorated graphene is exposed to hydrogen molecules, the phase of the palladium nanoclusters changes from Pd to Pd hydride (PdHx). The phase transfer decreases the work function and facilitates the flow of more electrons, resulting in a decrease of the resistance (Fig. 2(c)).

Although gold in the form of atoms and molecules is one of the most inactive noble metals, Au nanoparticles with sizes of less than 10 nm have ideal catalytic activity when supported on metal oxide or graphene-based materials [36,37]. Diverse studies on utilizing the catalytic activity of Au nanoparticles have investigated various aspects, such as surface modification and heterostructure formation. Unlike platinum and palladium nanoparticles, which have shown a remarkable enhancement of the hydrogen detection, no research on improving the hydrogen sensing properties of Au nanoparticles has been reported so far. In 2019, Kim *et al.* reported the enhancement of the room-temperature hydrogen sensing properties of a graphene-based sensor by using a Au-decorated graphene microchannel. Three-layer graphene was prepared by the CVD method and micropatterned to form a narrow micro-sized graphene channel [38]. Three-layer graphene was then transferred to a flexible and transparent polyimide substrate for the fabrication of the self-activated graphene-based gas sensor. Au (1 nm) was deposited on the graphene microchannel using an electron beam evaporator and agglomerated by Joule heating to form Au nanoparticles. Figs. 3(a) and (b) show a comparison of the hydrogen sensing behaviors of the Au-decorated graphene sensor and the pristine graphene sensor upon exposure to 50 ppm H_2 in the self-activation state. The Au-decorated graphene sensor exhibited a sensing response that is 48.8 times larger than that of the pristine graphene sensor, indicating that the Au nanoparticle decoration selectively enhanced the hydrogen sensing performance. First-principles density functional theory (DFT) calculations were performed for various geometries to understand the unusual enhancement of hydrogen sensing by Au decoration. The DFT analysis showed that the adsorption energies of the hydrogen atoms are notably high at the vertex and interface vertex sites of the Au nanoparticles, resulting in enhanced hydrogen detection despite the binding of hydrogen gas to the Au or graphene surface being energetically unfavorable (Figs. 3(c) and (d)). The sensing parameters of the several graphene-based hydrogen gas sensors and the commercial hydrogen gas sensor are summarized and listed in Table 1. More studies are needed for the commercialization of the graphene-based hydrogen sensors, especially the graphene-based sensors without incorporation of the metal-oxide semiconductors.

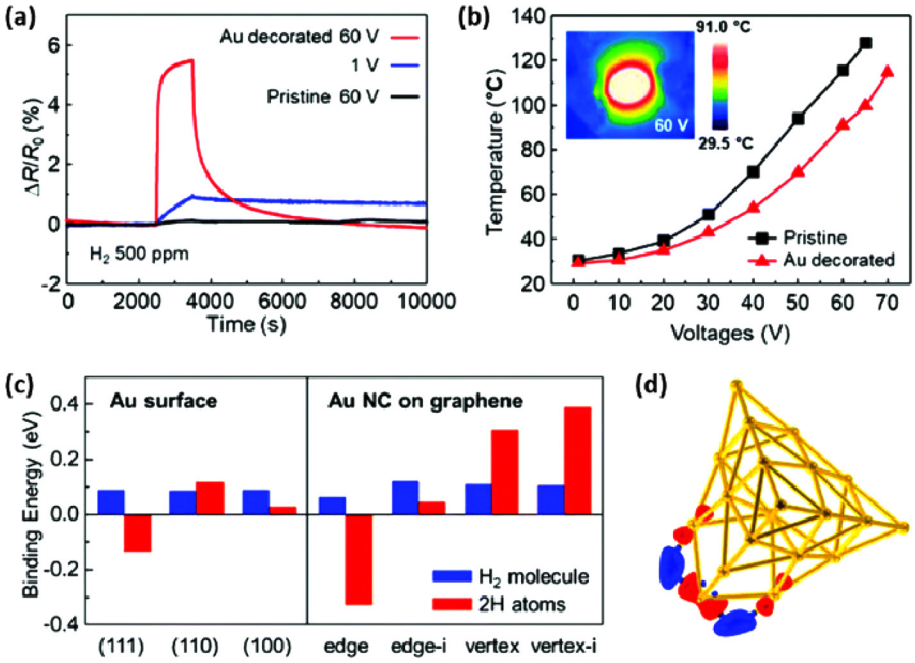

Fig 3. (a) Response curves of Au-decorated and pristine graphene sensors under different voltages. (b) Thermographic images and measured temperatures of Au-decorated and pristine graphene sensors. (c) Binding energies of hydrogen molecules and hydrogen atoms on (111), (110), and (100) Au surfaces and edge, interface edge (edge-i), vertex, and interface vertex (vertex-i) sites adsorption sites in Au nano-clusters on graphene. (d) Schematic of the charge density after adsorption of hydrogen atoms. Reprinted with permission from [38]. Copyright © 2019, Royal Society of Chemistry.

Table 1. Gas sensing performances of room temperature H_2 gas sensor based on graphene

Material	Gas concentration	Sensitivity (%)	Response time (s)	Recovery time (s)	Ref.
SnO_2/Graphene	100 ppm	300	1.1	1.2	25
ZnO/Graphene	100 ppm	28.1	30	38	26
Pt/Graphene	4 vol%	16	540	-	34
Pd/Graphene	100 ppm	17	-	-	35
Au/Graphene	500 ppm	5.4	16	274	38
SnO_2	100 ppm	90	-	-	(TGS821, Figaro, Inc., USA)

3. CONCLUSIONS

In this paper, we reviewed chemoresistive H_2 gas sensors based on 2D graphene. Because of the low response of graphene to H_2 molecules, various strategies have been suggested to enhance the selectivity of graphene. Metal oxide decoration and noble metal decoration are the most favored methods for the real-time detection of H_2. By decorating graphene with metal oxides such as SnO_2 and ZnO on graphene, the selectivity was improved so that H_2 resulted in the largest response among the various target gases. Moreover, noble metal decoration on graphene efficiently enhanced the gas response to H_2. Pt, Pd, and Au nanoparticles on the graphene surface, which acted as active sites for H_2 adsorption and catalytic effects. In particular, Au-decorated graphene exhibited a response to H_2 molecules that is 48.8 times larger than that of pristine graphene. Overall, metal oxide decoration and noble metal decoration are significantly effective strategies for controlling the selectivity and enhancing the gas response to H_2. We believe that these strategies will expand the applications and practical use of graphene for next-generation technologies.

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