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Authors: Junyoung Seo, Yeongjin Lim, Heungjoo Shin



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# Self-heating hydrogen gas sensor based on an array of single suspended carbon nanowires functionalized with palladium nanoparticles

Junyoung Seo, Yeongjin Lim, Heungjoo Shin\*

*Department of Mechanical Engineering, Ulsan National Institute of Science and Technology (UNIST),  
Ulsan, Republic of Korea*

E-mail: hjshin@unist.ac.kr

Phone: +82-52-217-2315

Address: 50 UNIST-gil, Eonyang-eup, Ulju-gun, Ulsan 44919, Republic of Korea

## **Research Highlights:**

- Hydrogen gas sensor based on an array of single suspended carbon nanowires decorated with Pd nanoparticles (PdNPs) of various sizes for room temperature H<sub>2</sub> gas sensing.
- Simple batch fabrication of composite suspended nanowire based gas sensor using carbon-MEMS and electrodeposition.
- Modulation of the sensitivity and range of the sensor by controlling Pd nanoparticle sizes.
- Wide sensing range by integrating nanowires with various sizes of PdNPs onto a chip.
- Quick and complete recovery of sensor signal in a very short time via ultralow-power, Joule heat-based self-heating.

## ABSTRACT

This study reports the development of a novel hydrogen gas sensor based on an array of single suspended carbon nanowires (diameter  $\sim 200$  nm, length  $\sim 100$   $\mu\text{m}$ ) decorated with Pd nanoparticles (PdNPs) of various sizes for room temperature  $\text{H}_2$  gas sensing. These sensors provide high sensitivity, a wide sensing range (10 ppm – 5 %), and complete gas response recovery in 5 s with ultralow power consumption (30  $\mu\text{W}$ ). Such performance is achieved using a novel suspended PdNP/carbon nanowire architecture, which offers enhanced mass transfer, high surface area to volume ratios, and good thermal insulation. This platform can be fabricated using simple batch microfabrication processes including carbon-MEMS and electrodeposition. The sensitivity and range of the sensor can be modulated by controlling Pd nanoparticle sizes (3 – 5 nm PdNPs: 3.2 %  $\text{ppm}^{-1/2}$ , 10 – 1,000 ppm; 10 – 15 nm PdNPs: 0.32 %  $\text{ppm}^{-1/2}$ , 700 ppm – 5 %). A wide sensing range is achieved by integrating nanowires with various sizes of PdNPs onto a chip. The electrical resistance of a suspended PdNP/carbon nanowire quickly and completely recovers its original state in a very short time via ultralow-power, Joule heat-based self-heating. This enables reproducible and long-term durable gas sensing.

## Keywords

Hydrogen gas sensors, Suspended carbon nanowires, Pd nanoparticles, Carbon-MEMS, Self-heating

## 1. Introduction

Hydrogen, a clean and sustainable energy source, has been used extensively in a variety of applications such as automobiles and fuel cells [1–3]. However,  $\text{H}_2$  gas requires special caution because of its low flammable limit of 4 % in air [4]. Therefore, it is important to develop  $\text{H}_2$  gas sensors with high sensitivity, fast response, fast recovery, and wide sensing ranges. Nanomaterials such as nanowires [5–

15], carbon nanotubes [16–18], nanorods [19, 20], and graphenes [21–27] have been actively investigated as materials for high performance  $H_2$  gas sensors.

Palladium (Pd) has been actively studied as a  $H_2$  sensor material because of its high  $H_2$  solubility at room temperature and  $H_2$ -dependent electrical conductivity.  $H_2$  molecules are adsorbed onto the surface of Pd via dissociation into hydrogen atoms, which diffuse into interstitial sites in the metal. The resulting solid solution of Pd and H ( $PdH_x$ ) increases the resistance of Pd at room temperature. However, Pd may be vulnerable to structural deformations due to  $PdH_x$  phase changes. The  $\alpha$  phase (solid solution of Pd and H) changes into a  $\beta$  phase (palladium hydride) when the  $H_2$  concentration increases [28]. To overcome this drawback and improve  $H_2$  sensitivity, sensor platforms have been developed based on variety of Pd nanostructures such as thin Pd films [15, 28, 29], amorphous Pd-alloy films [30–32], nanoporous Pd films [33], Pd nanowires [9–11], Pd nanoclusters [24], and Pd nanoparticles [16, 18, 23, 25, 34].

In our previous study, we developed a novel  $H_2$  gas sensor based on an individual, suspended carbon nanowire functionalized with a thin Pd film [15]. Owing to the suspended architecture of the carbon-nanowire template and  $SiO_2$  eaves, a single metal coating process enabled the selective Pd deposition on the carbon nanowire. For structural robustness and high sensitivity, a very thin layer ( $\sim 5$  nm) of Pd was coated on the carbon nanowire. However, this thin Pd layer limited gas absorption, and thus the gas response was saturated even at relatively low  $H_2$  concentrations ( $\sim 500$  ppm). In addition, although the actual sensor area was at the nanoscale, the whole top surface of the substrate had to be coated with a Pd layer resulting in the material waste. In addition to fast saturation, the Pd film-based  $H_2$  sensor exhibited slow resistance recovery because of the limited diffusion of hydrogen atoms at room temperature. This slow resistance recovery limits precise and continuous detection of fluctuating  $H_2$  concentrations. The PdNP/carbon nanowire based gas sensor shown in Fig. S1 also exhibits this problem. Due to slow solid diffusion, previously absorbed H atoms are not completely removed before the next  $H_2$  gas injection. This limitation can be overcome by increasing the diffusion rate of hydrogen atoms in bulk Pd by heating the gas sensor. However, relatively high power consumption occurs even with small devices because the entire sensor chip must be heated.

Recently, studies of fast gas response and recovery with low power consumption have been introduced [11, 13, 14, 17, 35, 36]. The researchers increased the temperatures of micro-/nano-sized sensors by allowing additional current to flow along the sensor structures, without integrating external heaters into the chip. Thus, the sensor structures could heat themselves via Joule heating. However, the previous studies still need to improve aspects of sensor performance such as the limit of detection (LOD), sensing range, and power consumption. In addition, cost-effective technologies for sensor fabrication must be incorporated.

In this work, we have overcome two significant limitations of Pd nanostructure-based H<sub>2</sub> sensors: fast gas response saturation or narrow sensing range, and slow resistance recovery. We fabricated arrays of individual carbon nanowires decorated with Pd nanoparticles using only simple batch microfabrication processes such as carbon-MEMS and electrodeposition. The suspended sensor architecture and large nanoparticle surface area to volume ratio enabled high-sensitivity H<sub>2</sub> detection with excellent detection limits and fast response times. Furthermore, the PdNP/carbon nanowire based sensor was capable of sensing a wide range of H<sub>2</sub> concentrations because the Pd nanoparticle size can be controlled by manipulating electrodeposition conditions such as deposition time and potential. For fast and complete resistance recovery, additional current was applied along the PdNP/carbon nanowire to facilitate self-heating. Because of the long, suspended geometry of the PdNP/carbon nanowires, there was very limited heat loss and only 5 s of ultra-low-power heating was required for complete and instant resistance recovery (Fig. 1).

In this paper, we introduce details of the sensor fabrication methods, including the carbon-MEMS and electrodeposition processes. Carbon-MEMS is a versatile batch microfabrication process which uses UV lithography-based polymer patterning and pyrolysis to create an array of single suspended carbon nanowires decorated with Pd nanoparticles of various sizes. The sensitivity and sensing range can be modulated by controlling the Pd nanoparticle size during electrodeposition. To ensure that the effect of PdNPs on the composite nanowire resistance dominates and produces a large H<sub>2</sub> gas response, the resistivity of the carbon nanowire was modulated by controlling the pyrolysis temperature. In addition,

reproducible  $\text{H}_2$  gas sensing capabilities driven by fast, complete gas response recovery are demonstrated.

## 2. Experimental

The fabrication steps used to make the suspended carbon nanowire functionalized with Pd nanoparticles are illustrated in Fig. S2. A 1  $\mu\text{m}$ -thick  $\text{SiO}_2$  insulation layer was grown on a 6-inch Si wafer (p-type, boron doped, 5 – 20  $\Omega\text{ cm}$ , thickness = 660 – 700  $\mu\text{m}$ ; LG Siltron Co., Ltd., Korea) via wet oxidation. Polymer precursor structures including suspended microwires were patterned using two successive UV lithography processes. For the patterning of polymer posts that supported the suspended microwires, a spin-coated 20  $\mu\text{m}$ -thick negative photoresist layer (SU-8 2025, Microchem. Corp., USA) was exposed from top to bottom. Upon the second UV exposure, suspended polymer microwires were polymerized only at the shallow top polymer region with a low dose. After a post-exposure bake step, the monolithic polymer structure, including suspended wires and their supporting posts, was defined in a single development process. The monolithic polymer precursor structures were converted into monolithic carbon structures via pyrolysis in vacuum. During pyrolysis, the photoresist structures shrank dramatically. Thus, the diameters of the suspended polymer wires decreased to nanometer scale while the suspended structures became elongated because of volume reduction in the post structures. Finally, Pd nanoparticles were grown on the suspended carbon nanowires via electrodeposition in a 1 mM Pd electrolyte solution,  $\text{Na}_2\text{PdCl}_4$  (98% purity, Sigma Aldrich Co., USA). During electrodeposition, the monolithic carbon structure was biased with various potentials (-0.6 – -1.5 V vs the Ag/AgCl pseudo-reference electrode) and a platinum wire was used as the counter electrode. After electrodeposition, the sensor chip was annealed at 100  $^\circ\text{C}$  in vacuum ( $1.0 \times 10^{-5}$  Torr) for 20 min using a rapid thermal process (KVR6000, Korea Vacuum Tech. Ltd., Korea).

The change in the electrical resistance of the suspended PdNP/carbon nanowire in response to  $\text{H}_2$  was measured at atmospheric pressure and room temperature in a gas chamber equipped with mass flow meters as illustrated in Fig. S3. Due to the limited flow rates of mass flow controllers and the laboratory safety rule, the  $\text{H}_2$  gas detection was performed for 10 ppm – 5 % of  $\text{H}_2$ . Before  $\text{H}_2$  gas detection, the

chamber was purged via several vacuum and N<sub>2</sub> purge cycles. Hydrogen concentrations were controlled by mixing 5 % H<sub>2</sub> in air with pure air using a gas flow controller (GMC1200, Atovac, Korea). While the H<sub>2</sub>/air gas mixture flowed through the gas chamber at room temperature, electrical current was applied through two carbon posts and the voltage drop along the PdNP/carbon nanowire was measured using a source meter (Keithley 2401, Keithley Instruments, Inc., USA). The input power was set to ~ 6.25 nW during the gas concentration measurement and then, increased to ~ 30  $\mu$ W for 5 s when the H<sub>2</sub> gas was closed resulting in fast and complete recovery.

The morphologies of suspended PdNP/carbon nanowires were characterized via SEM (Quanta 200, FEI Company, USA). The microstructures and crystallinities of Pd nanoparticles coated on a suspended carbon nanowire were characterized via HRTEM (JEM-2100F, JEOL Ltd., Japan). The TEM sample was prepared using a focused-ion-beam (FIB) milling machine (Helios 450HP, FEI company, USA). To reduce Ga ion-induced damage to the Pd nanoparticles, an extra Pd layer was electrodeposited.

### 3. Results and discussion

#### 3.1. Morphologies of electrodeposited Pd nanoparticles

To understand the effects of electrodeposition parameters such as potential and deposition time, systematic deposition of Pd nanoparticles was performed. First, the effect of electrical potential on the nanoparticle morphology was characterized by applying various levels of potential (-0.4, -0.8, and -1.2 V vs Ag/AgCl) to suspended carbon nanowires (diameter ~ 200 nm, length ~ 100  $\mu$ m) for 5 s. The number of Pd nucleation sites increased with the applied potential, and thus the carbon nanowire became uniformly coated with Pd seed particles at -1.2 V, as shown Fig. S4. After the nucleation step (-1.2 V for 5 s), the nanoparticle size was controlled by manipulating the electrodeposition time. For nanoparticle size control, the electrodeposition step used lower a potential (-0.8 V vs Ag/AgCl) than the nucleation step. In this study, two different sizes of PdNPs were deposited on suspended carbon nanowires. The growth conditions of the composite wires were varied and the samples were named NW1 and NW2 (NW1: -1.2 V for 5 s and -0.8 V for 5 s, NW2: -1.2 V for 5 s and -0.8 V for 25 s). The sizes of the Pd nanoparticles increased with the growth step deposition time. Thus, uniform coating

with two different sizes of PdNPs occurred, as shown in Fig. 2. In this research, the H<sub>2</sub> gas sensing performances of these two types of suspended PdNP/carbon nanowires were characterized.

The crystallinities and microstructures of PdNPs grown on suspended carbon nanowires were characterized via HR-TEM as shown in Fig. S5. We prepared PdNPs larger than those used in NW1 and NW2 (~ 70 nm) because small PdNPs are easily damaged during FIB sample preparation. The TEM image and well-defined fringe patterns indicate that the PdNPs are highly crystallized (Fig. S5(c)). The interplanar spacings of the Pd lattice fringes are 0.23 and 0.2 nm, which correspond to the (111) and (200) lattice planes, respectively, of the face-centered cubic (fcc) Pd structure.

### *3.2. Characterization of the electrical properties of suspended PdNP/carbon nanowires*

The change in the electrical resistance of suspended PdNP/carbon nanowires after nanoparticle deposition was characterized. The total electrical resistance of the composite nanowire is determined by the resistance of the carbon core wire and the surrounding Pd nanoparticles. Pd nanoparticles are dispersed on the carbon nanowire, so charge carriers entering the suspended composite nanowire have little opportunity to pass through the Pd nanoparticles unless their resistance is significantly smaller than that of carbon. The ratio of the resistance of Pd nanoparticles to that of carbon nanowires must be reduced so that the nanoparticles can transport charge carriers (Fig. 3(a)). The electrical conductivity of pyrolyzed carbon is determined by the graphitic composition ratio, which increases with the pyrolysis temperature [37]. Thus, the pyrolysis temperature can modulate the electrical conductivity of suspended carbon nanowires, as shown in Fig. S6. Details of the relationship between pyrolysis temperature and electrical conductivity have been described in detail elsewhere [38]. Suspended carbon nanowires pyrolyzed at 700 °C, which exhibited the lowest conductivity as shown in Fig. S6, were selected as the H<sub>2</sub> gas sensor platform for this study. Electrodeposition of PdNPs reduced the electrical resistance of the suspended composite nanowires by 3.5 and 15 times for NW1 and NW2, respectively. Both of the composite nanowires exhibited good Ohmic contact, as shown Fig. 3(b).



### 3.3. Characterization of $H_2$ gas sensing performance

As previously mentioned, Joule-heat-based self-heating was used to enhance kinetic interactions between gas molecules and the sensor surface. Thus, the increase in resistance caused by gas absorption could be recovered instantaneously. Because of the sub-micrometer diameter of the suspended PdNP/carbon nanowire, and because the delicate nanowire is detached from the substrate, measurement of changes in the temperatures of the suspended nanowires is limited. Instead, the effect of the self-heating was evaluated by comparing the resistance recovery rates of a suspended PdNPs/carbon nanowire under various heating scenarios, as shown in Fig. 4. In this experiment, a suspended carbon nanowire decorated with large Pd nanoparticles (NW2) was exposed to 1,000 ppm of  $H_2$ . The wire was heated using via either self-heating or an external heater for 5 s upon closing the  $H_2$  gas line. The resistance of the composite nanowire recovered faster at higher external heater temperatures. In particular, the resistance completely recovered after a short time with an external heater at 55 °C. Nearly the same resistance recovery behavior was exhibited when the PdNP/carbon nanowire was heated by 30  $\mu$ W of self-heating. This experiment demonstrates the feasibility of suspended composite nanowires as  $H_2$  gas sensors capable of complete, instantaneous gas response recovery and precise  $H_2$  detection, without the signal drift that is frequently exhibited by sensors with slow recovery rates.

Fig. 5 (a) and (b) show the resistances of NW 1 and NW2 with hydrogen concentrations that vary from 5 % to 10 ppm, at room temperature. In this experiment, the composite wires were heated for 5 s by Joule heating at each gas injection period. The composite nanowire with small PdNPs (NW1, diameter: 3 – 5 nm) exhibited a larger gas response ( $\Delta R/R$ ;  $\Delta R$  = change in resistance after  $H_2$  gas injection,  $R$  = resistance before  $H_2$  gas injection; e.g.  $\Delta R/R$  = 185 % at 2.5 %  $H_2$ ) than that ( $\Delta R/R$  = 61 % at 2.5 %  $H_2$ ) of the nanowire with large Pd nanoparticles (NW2, diameter: 10 – 15 nm). The gas response of NW1 increased quickly and linearly with the square root of the  $H_2$  concentration. However, it started to saturate from 1,000 ppm of  $H_2$  (Fig. 5(a) and (c)). In contrast, NW2 exhibited a linear gas response from 700 ppm to 5 % of  $H_2$  (Fig. 5(b) and (c)), despite having lower sensitivity than NW1. The sensitivities calculated from linear fitting of the curves in the gas response data are 3.2 % ppm<sup>-1/2</sup> from 10 – 1,000 ppm and 0.32 % ppm<sup>-1/2</sup> from 700 ppm – 5 % for NW1 and NW2, respectively. The gas sensing

behaviors of the PdNP/carbon-nanowires indicate that sensing capabilities, including sensitivity and sensing range, are closely related to nanoparticle sizes. The resistances of small PdNPs (NW1) increased more rapidly with H<sub>2</sub> injection because of their larger surface area to volume ratios. However, the gas response of NW1 became saturated at lower concentration because of the small volume of PdNPs in the composite. In contrast, NW2 exhibited a wider sensing range than NW1, but did not exhibit a linear gas response relationship at low H<sub>2</sub> concentrations. NW2 was not sensitive enough to detect H<sub>2</sub> at low concentrations because of the small surface area to volume ratios dictated by large particle sizes.

The linear relationship between the gas response and the square root of hydrogen concentration can be understood by applying the Langmuir adsorption isotherm theory to dissociation of hydrogen molecules upon adsorption on the Pd nanoparticle surface [39]. H<sub>2</sub> dissociation on Pd nanoparticle surface can be described via Equation (1).



The adsorption and desorption rates of hydrogen are expressed as  $k_1 p(1-\theta)^2$  and  $k_{-1}(\theta)^2$  where  $k_1$  and  $k_{-1}$  are the adsorption and desorption constants, respectively. In these expressions,  $p$  is the partial pressure of H<sub>2</sub> and  $\theta$  is the fraction of Pd surface sites occupied by adsorbed hydrogen. At equilibrium, the adsorption and desorption rates are equal, and thus the ratio of the occupied to non-occupied surface sites is proportional to the square root of the partial pressure. This is described in Equation (2).

$$k_1 p(1-\theta)^2 = k_{-1}(\theta)^2 \quad \text{or} \quad \frac{\theta}{1-\theta} = \left( \frac{k_1}{k_{-1}} \right)^{1/2} p^{1/2} \quad (2)$$

At low concentrations of H<sub>2</sub> ( $\theta \ll 1$ ), the ratio of occupied to non-occupied surface sites is proportional to the square root of the partial pressure or concentration of H<sub>2</sub>. Therefore, it can be assumed that the gas response of the PdNP/carbon nanowire is closely related to chemisorption, as described by Equation (3):

$$\Delta R / R \propto \theta \approx (k_1 / k_{-1})^{1/2} p^{1/2} \quad (3)$$

The response times of NW1 and NW2 at various hydrogen concentrations are shown in Fig. 5(d). The response time is defined as the time required for the sensor to reach  $e^{-1}$  (~36.8 %) of the maximum resistance change after H<sub>2</sub> exposure [25]. Both types of composite nanowires (NW1 and NW2) exhibited fast gas responses at room temperature (< 70 s). At low gas concentrations,  $\theta$  is insignificant so the adsorption rate is linearly proportional to the gas concentration. The adsorption rate is then gradually affected by the  $(1 - \theta)^2$  term as the gas concentration increases. Thus, the initial response time is inversely proportional to the gas concentration. The response time curve of NW1 exhibits good agreement with this inverse relationship at low concentrations (10 – 1,000 ppm), but the time required for gas response gradually increases with the gas concentration because the surface sites available for hydrogen adsorption become depleted. However, the composite nanowire decorated with large PdNPs (NW2) exhibits an inverse relationship at relatively high gas concentrations (700 ppm – 5 %) because of its long diffusion path and small surface area to volume ratio. At H<sub>2</sub> concentrations lower than 1,000 ppm, NW1 responds faster than NW2. This relationship is reversed at high H<sub>2</sub> concentrations (> 1,000 ppm). With small Pd nanoparticles, dissolution of hydrogen into bulk Pd occurs efficiently, even at low gas concentrations because of the large surface area to volume ratios involved. However, the Pd particles easily become saturated with hydrogen because of their small size. Large Pd nanoparticles exhibit slow responses because of their relatively small surface area to volume ratios, but saturation is delayed because the particles are larger. The reproducibility and reliability of the PdNP/carbon-nanowire-based H<sub>2</sub> gas sensors were evaluated by cycling H<sub>2</sub> gas injection and purging steps with various gas concentrations, as shown in Fig. 6. Both NW1 and NW2 exhibited similar gas responses at the same H<sub>2</sub> concentrations after several gas injection cycles. This indicates the ability of the gas sensors to provide precise, continuous detection of H<sub>2</sub> gas concentrations.

The long-term durability of the gas sensor was tested by cycling injection of H<sub>2</sub> to the gas sensor for 30 days without self-heating. As previously mentioned, complete recovery of the gas response requires significant time because of slow solid diffusion at room temperature. In addition, humidity and

contaminants deplete the available Pd surface sites and thus the gas response reduces as the operating time increases [40]. Without self-heating, the sensor signal of the PdNPs/carbon nanowire (NW1) was degraded and became deteriorated over time, as shown in Fig. 7. However, application of 5 s of self-heating to the composite nanowire completely recovered its gas response capability, even after 30 days of sensor operation.

Table S1 compares the present PdNPs/carbon-nanowire-based H<sub>2</sub> sensor with previously reported resistive hydrogen sensors. Metal-oxide-nanomaterial based sensors exhibited extraordinarily high gas responses but the linear sensing range were limited or high power was required for the sensor operation [20, 26, 27, 41]. N. Pinna *et al.* reported a hydrogen gas sensor with fast response and recovery times using platinum/tin oxide/reduced graphene oxide heteronanostructures. The heteronanostructure-based sensor could be operated at relatively low temperature (50 °C) but it could detect high H<sub>2</sub> concentrations (> 5,000 ppm) [27]. Although H<sub>2</sub> sensors based on palladium nanomaterials could work at room temperature, the gas response became saturated at relatively low concentrations [12, 15, 18, 22–25]. Self-heating based H<sub>2</sub> exhibited fast response and recovery with low power consumption but relatively low response, limited sensing range, and cumbersome fabrication have to be overcome [11, 13, 36]. The present PdNPs/carbon-nanowire-based sensor exhibited good gas response and response time comparable to other Pd-nanomaterial-based sensors but linear sensing range could be extended to 10 ppm–5 % by the integration of nanowire array on a substrate. Moreover, the sensor resistance could be completely recovered to its original value in 5 s with ultra-low power with a highly reproducible manner owing to suspended nanowire architecture. Furthermore, the suspended sensor arrays were fabricated at a wafer-level using only conventional microfabrication technologies ensuring high throughput and reproducibility.

#### 4. Conclusions

We have developed a novel gas sensor based on an array of individual, suspended carbon nanowires decorated with PdNPs of various sizes for room temperature H<sub>2</sub> gas sensing with high sensitivity, a

wide linear sensing range (10 ppm – 5 %), and complete recovery in 5 s via low power consumption self-heating. These suspended PdNP/carbon nanowires were fabricated using conventional batch microfabrication methods enabling cost-effective wafer-level sensor chip production. The electrical resistances of PdNP/carbon nanowires were dominated by the PdNPs because charge carriers flow preferentially via PdNPs due to the relatively low electrical conductivities of the carbon nanowires. The sensitivity and linear sensing range of the H<sub>2</sub> sensor were modulated by controlling the sizes of the PdNPs. Thus, a wide range of H<sub>2</sub> gas sensing capabilities can be facilitated by building an array of single suspended carbon nanowires integrated with PdNPs of various sizes. Furthermore, due to their suspended architecture, the resistances of the PdNP/carbon nanowires were quickly and completely recovered via ultra-low-power, Joule heat-based self-heating. This unique recovery capability also enabled highly reproducible and long-term H<sub>2</sub> gas sensing without calibration. The suspended PdNP/carbon nanowires exhibited excellent feasibility as a high performance H<sub>2</sub> detection and monitoring tool with the advantages of cost-effective nanofabrication.

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## Author Biographies

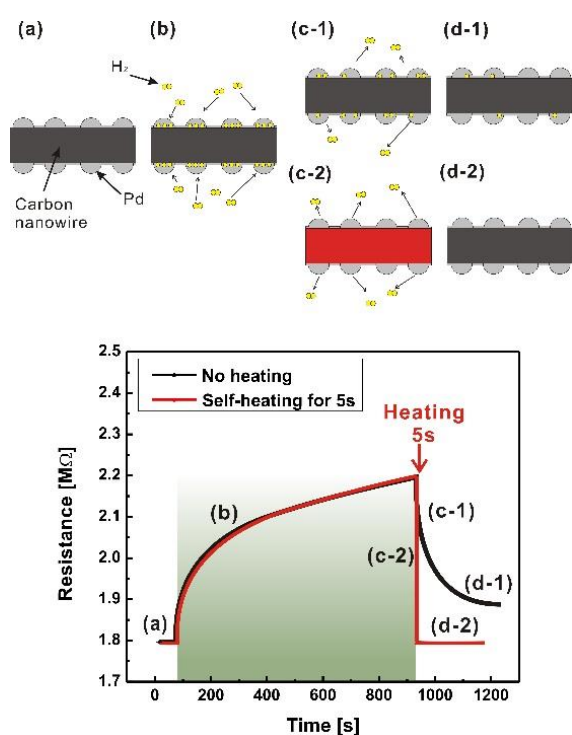
**Heungjoo Shin** received his B.S. (1998) and M.S (2000) from the Department of Mechanical Design and Production Engineering in Seoul National University, and Ph.D (2006) from the Department of Mechanical Engineering in Georgia Institute of Technology. He worked as a postdoctoral fellow in Advanced Sensors Laboratory of School of Chemistry and Biochemistry at the Georgia Institute of Technology from 2006 to 2008. He joined the Ulsan National Institute of Science and Technology in 2009 and he is currently an associate professor in the School of Mechanical and Nuclear Engineering at the same school. His research interests include the development of pyrolytic micro/nano carbon structure based gas/electrochemical/biosensors, SECM-AFM probes, and micro/nanofabrication technologies.

**Junyoung Seo** received his B.S. (2015) from the School of Mechanical and Nuclear Engineering in Ulsan National Institute of Science and Technology. He is currently pursuing Ph.D. degree in the School of Mechanical and Nuclear Engine in Ulsan National Institute of Science and Technology. His research topic is the development of Pd/carbon-nanostructure-based gas sensors.

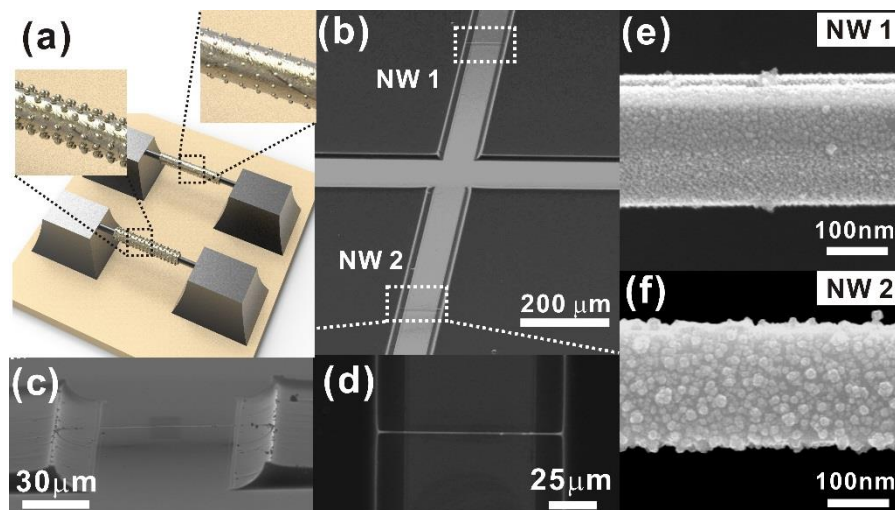
**Yeongjin Lim** received his B.S. (2009) from the Department of Material Science and Engineering in Gyeongsang National University. He is currently pursuing Ph.D. degree in the School of Mechanical and Advanced Materials Engineering in Ulsan National Institute of Science and Technology. His research topic is the development of gas sensors based on 3D functionalized carbon nanostructures.

## Figure captions

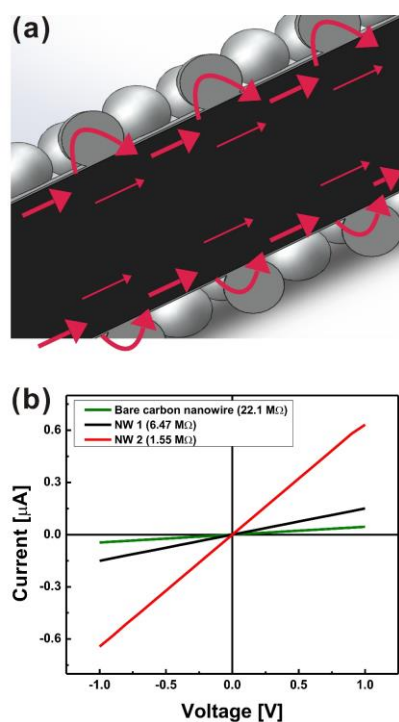
**Fig. 1.** Schematic of the  $H_2$  gas sensing and self-heating recovery processes of a PdNP/carbon nanowire: (a) Initial state, (b)  $H_2$  sensing (gas input), (c, d) Recovery (gas removal); (c-1) no heating (c-2) self-heating, (d-1) slow recovery, (d-2) fast and complete recovery.



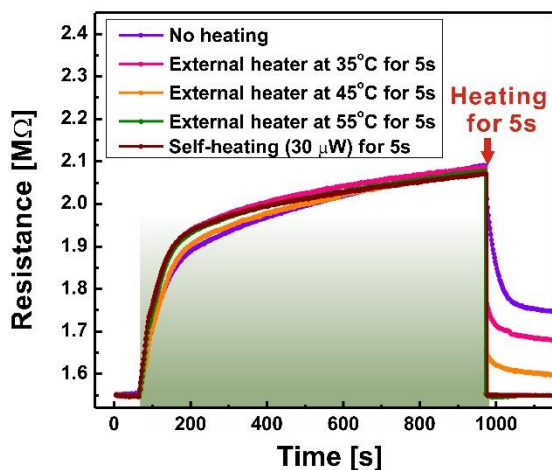
**Fig. 2.** (a) Schematic and (b) SEM images of an array of two different types of single suspended PdNP/carbon nanowires integrated onto a single chip. (c) Bird's-eye view and (d) top view of a suspended PdNPs/carbon nanowire (diameter  $\sim 200$  nm, length  $\sim 100$   $\mu\text{m}$ ). Enlarged views of (e) small PdNPs (NW1, diameter: 3 – 5 nm) and (f) large PdNPs (NW2, diameter: 10 – 15 nm).



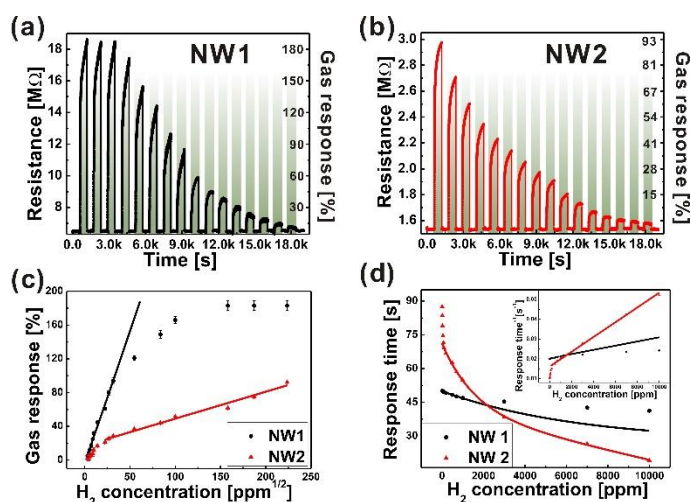
**Fig. 3.** (a) Schematic image of the flow (red arrows) of electrical current through a PdNP/carbon nanowire. (b) I-V characteristics of a suspended carbon nanowire before and after Pd nanoparticle deposition.



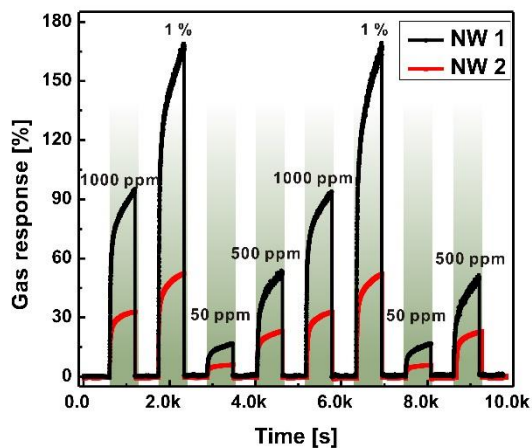
**Fig. 4.** Gas response recovery behavior of a carbon nanowire coated with large PdNPs (NW2, PdNP diameter: 10 – 15 nm) under various heating conditions such as no-heating, external heating, and self-heating. The green shaded area indicates injection of 1,000 ppm of  $H_2$ .



**Fig. 5.** Real-time electrical resistance and gas response curves of PdNP/carbon nanowires ((a) NW1, PdNP diameter: 3 – 5 nm, (b) NW2, PdNP diameter: 10 – 15 nm) with various amounts of  $H_2$  (green shaded blocks indicate 5, 3.5, 2.5, 1, 0.7, and 0.3 %, and 1,000, 700, 500, 200, 100, 80, 50, 30, 20, and 10 ppm respectively) mixed into air at room temperature. (c) Gas responses of NW1 and NW2 versus the square root of  $H_2$  concentration. (d) Response time versus  $H_2$  concentration (the inset graph is the reciprocal of response time vs.  $H_2$  concentration).



**Fig. 6.** Reproducible gas responses of suspended PdNP/carbon nanowires (NW1, PdNP diameter: 3 – 5 nm; NW2, PdNP diameter: 10 – 15 nm) during multiple injection-purging cycles with various concentrations of  $H_2$ .



**Fig. 7.** Long-term durability test: the gas response and recovery behaviors of a suspended carbon nanowire coated with small PdNPs (NW1, PdNP diameter: 3 – 5 nm) tested once a day for 1 h in the period of 30 day. Green shaded areas indicate the injection of 1,000 ppm of  $H_2$ . Red arrows indicate self-heating for 5 s.

