Flexible hydrogen sensors using graphene with palladium nanoparticle decoration

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ABSTRACT

Flexible hydrogen gas (H_2) sensors are fabricated using a single layer graphene decorated with palladium (Pd) nanoparticles. Thermally evaporated Pd is generally deposited on a graphene in the form of nanoparticles when the deposition thickness is very small. The graphene sensor with Pd thickness of 3 nm exhibits a gas response of ~33% when exposed to 1000 ppm H_2 and it is able to detect as low as 20 ppm H_2 at room temperature (22 °C). The sensor is so flexible that any significant degradation is not observed when it is bent to a curved geometry with a bending radius of 3 mm. The flexible hydrogen sensors are applicable to a broad range of systems with demanding mechanical flexibility, durability and high gas response.

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1. Introduction

The interest in hydrogen sensors has been increased in diverse applications related to hydrogen technologies including hydrogen purification, storage and fuel cell [1–4]. Most of commercially available hydrogen sensors are composed of metal oxide (e.g., tin oxide) films based on chemiresistive detection [5–9]. However, the metal oxide sensors usually require heating over 400 °C to yield satisfactory results [9,10]. Recently, palladium (Pd) or its alloy have been proposed as an alternative to metal oxide because they exhibit both high gas response and selectivity in hydrogen sensing at room temperature [11–13]. The absorption of hydrogen atoms results in the formation of Pd hydride, leading to the changes of physical properties, such as work function, electrical resistance, mechanical strain, and phase transition. Chemiresistive method utilizing the change in work function of Pd upon exposure to hydrogen has been extensively investigated due to their superior gas response, real-time detection and low-power consumption.

Graphene has definite advantages over other gas sensing materials. It is a perfectly two-dimensional atomic material, and therefore, has maximum surface area with respect to its volume. Therefore, graphene decorated with Pd nanoparticles is a promising combination for hydrogen sensing material due to its large specific surface area for molecular adsorption and outstanding electrical properties of graphene such as low noise level and high carrier mobility [14,15]. Results with graphene–Pd sensing materials, such as graphene deposited with Pd nanoparticles on SiO_2/Si substrate [16], Pd-functionalized multi-layer graphene nanoribbon networks [12] and graphene/Pd nanocomposite [17], were demonstrated for hydrogen sensors. Theoretical studies also revealed the mechanism of atomic and molecular hydrogen adsorption onto Pd-decorated graphene monolayer [18].

In the present study we fabricated a hydrogen sensor based on graphene decorated with thermally evaporated Pd nanoparticles. Thermal evaporation deposits palladium on a graphene in the form of nanoparticles when the thickness is very small. The optimized graphene sensor with 3 nm-thick Pd exhibits a gas response of ~33% when exposed to 1000 ppm H_2 at room temperature (22 °C). Moreover, the fabricated sensor operates well when it is bent to a curved geometry with a bending radius down to 3 mm. The flexible hydrogen sensors are applicable to a broad range of system demanding high mechanical durability and gas response, such as wrapping over hydrogen pipelines.

2. Experimental setup and fabrication

Graphene films were grown on 25 μm-thick copper (Cu) foils (Alfa Aesar, item no. 13382) using CVD method [19]. The Cu foil was annealed at 1000 °C and low pressure with a H_2 flow of 6 sccm
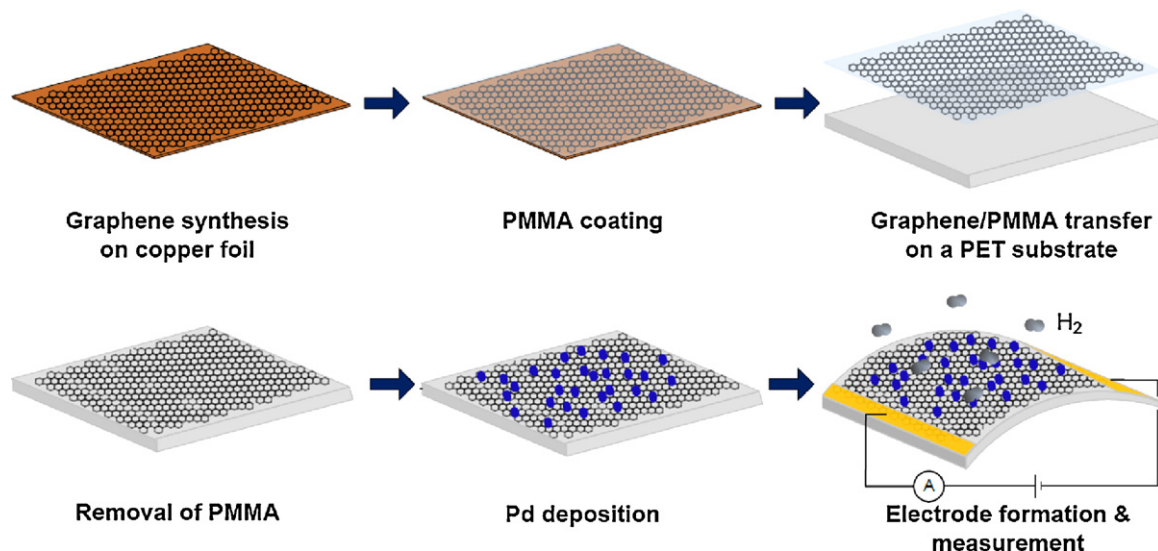
Fig. 1. Schematic drawing of the fabrication procedure of the hydrogen gas sensor.

for 30 min, and then graphene growth was carried out in succession at the same temperature by introducing CH_4:H_2 (105:6 sccm) gases for 20 min. After the growth process, the furnace was cooled down to room temperature with maintaining the gas flow.

For a gas sensing tests, gold (Au) lead wires were connected to the electrode of graphene sensor using silver (Ag) paste, and the fabricated sensor was placed in a quartz tube with a gas inlet and outlet. The sensor was exposed to dry N_2 (500 sccm) for 10 min to record an initial sensor resistance, and then H_2 balanced with N_2 were injected for 15 min to measure the sensing signal. To recover the sensor, N_2 was supplied into the tube for 30 min. The use of dry N_2 as a carrier gas enables us to exclude the effect of other reactive gas molecules, especially oxygen [20,21].

The resistance changes of the sensor were measured using a multimeter (2000 multimeter, Keithley, USA).

The fabrication procedure of the hydrogen gas sensor is schematically described in Fig. 1. Single layer graphene was grown on both sides of the copper foil using chemical vapor deposition (CVD) method. After the synthesis, one side of the copper foil specimen was spin-coated with poly-methyl methacrylate (PMMA) to mechanically support the graphene layer during its transfer process to a substrate. The graphene layer on the other side was removed by oxygen plasma treatment, and then the specimen was floated on the surface of iron chloride aqueous solution to separate the graphene/PMMA layer from the specimen by etching the copper foil. The floating graphene/PMMA layer was subsequently transferred onto a polyethylene terephthalate (PET) substrate. The substrate was cut into a piece with the dimension of 20 mm × 10 mm, and then the PMMA layer was removed by immersing the substrate in chloroform. Palladium deposition was performed on the graphene with the thickness ranging from 1 to 10 nm using thermal evaporation. Finally, gold lead wires were connected to the graphene sensor using silver paste for the gas sensing measurements.

Fig. 2(a) represents the Raman spectroscopy result which clearly indicates that the prepared graphene has a single layer with 2D/G peak ratio of 3.3 [19,22]. Fig. 2(b) shows the initial resistances (R_o) of each device with respect to the Pd deposition thickness. The resistance of the graphene decreases as the Pd thickness increases, and the rapid decrease of the resistance is observed when the Pd thickness is about 5 nm. The deposited Pd nucleates and grows into individual nanoparticles on graphene surface as shown in atomic force microscopy (AFM) images of Fig. 2(c). It is a well-known film growth mechanism in metal deposition process on a substrate,

where cohesive bonds between metal atoms are stronger than adhesive bonds between the atoms and substrate [23]. It is noteworthy in this regard that the surface energy of graphene is quite low (46.7 mJ/m^2) [24], thus the Pd nanoparticles are effectively formed on the graphene surface.

3. Performance evaluation of the sensor

We investigated the performance of the sensors in terms of gas response and response time. Gas response is defined by the percentile resistance change when the sensor is exposed to a gas as follows:

$$\text{Gas response} \ (\%) = \frac{R_g - R_o}{R_o} \times 100 \tag{1}$$

where R_o and R_g are the resistances of the sensor before and after the exposure to a gas, respectively. Response time is defined as the time required for the sensor to reach e^{-1} (∼36.8%) of the maximum resistance change after the sensor is exposed to gas molecules [11]. All measurements were carried out at room temperature.

The density of Pd nanoparticles, which can be controlled by Pd deposition thickness, is critical to the sensing performance. Fig. 3 shows the relative resistance changes of the graphene sensors exposed to 1000 ppm concentration of hydrogen gas. While no detectable change in resistance was observed in pristine graphene during hydrogen injection, the Pd decorated graphene sensors exhibits significant resistance changes as shown in the figure. When the sensor is exposed to hydrogen, the composition of the Pd nanoparticles on the surface of graphene is changed into palladium hydride that possesses lower work function than pure Pd [12,25]. The lower work function associated with palladium hydride is beneficial to the transfer of more electrons from the Pd nanoparticles to the graphene, which leads to trap the p-type carriers in the graphene, resulting in an increase of resistance of the device.

The gas responses of the sensors are plotted with respect to the Pd deposition thickness in the inset of Fig. 3. The gas response gradually increases and reaches the maximum value of 32.9% for the sensor with 3 nm-thick Pd. It is reasonable that the improved sensing responses may attribute to the increased coverage of Pd nanoparticles on graphene surface [26]. However, the sensor with thicker Pd film exhibited lower gas responses due to a major conduction path through the Pd film rather than graphene electrical channel. Since the optimized density of Pd nanoparticles, which
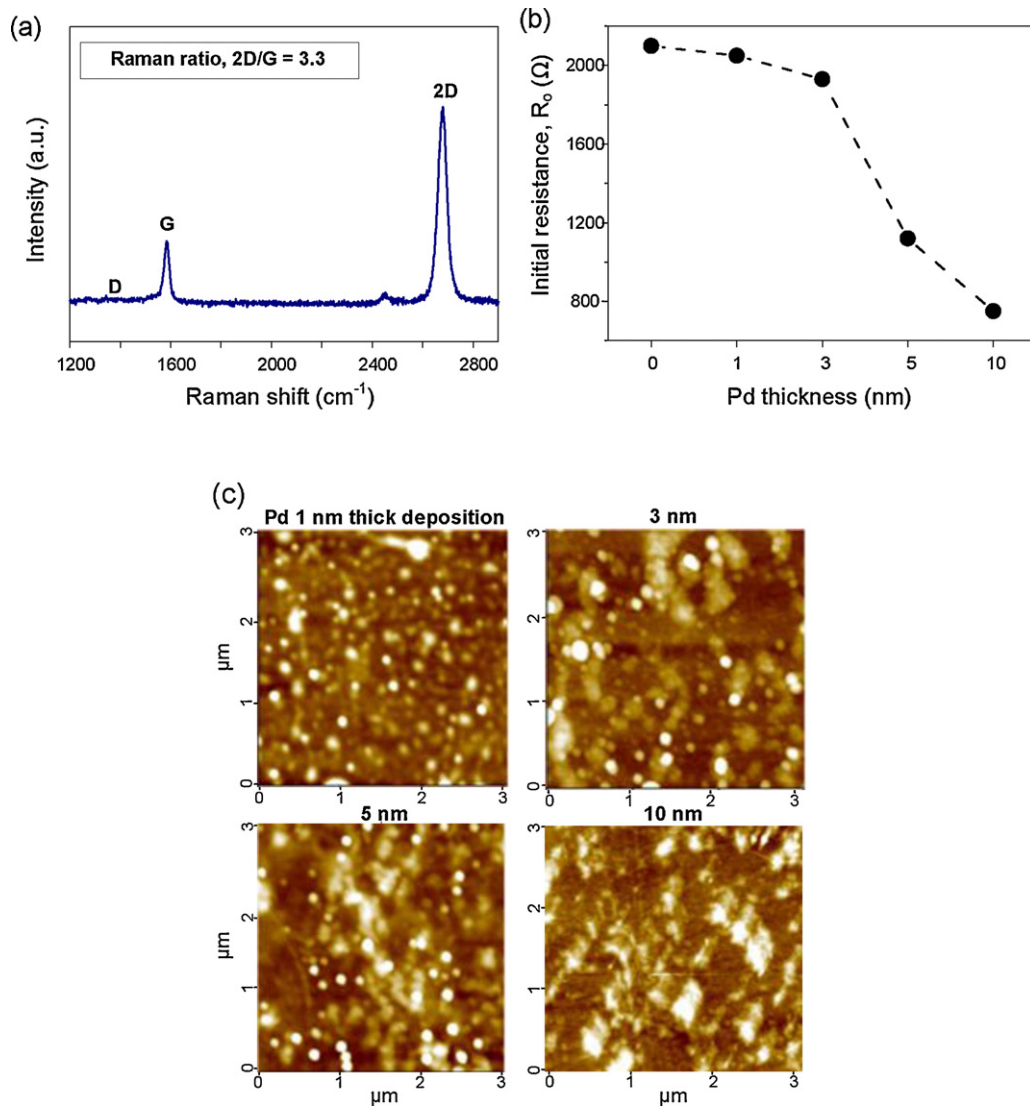
Fig. 2. (a) Raman spectrum of the transferred graphene on a PET substrate. (b) The initial resistances of the graphene sensor with respect to Pd deposition thickness. (c) AFM images of the Pd deposited graphene surface.
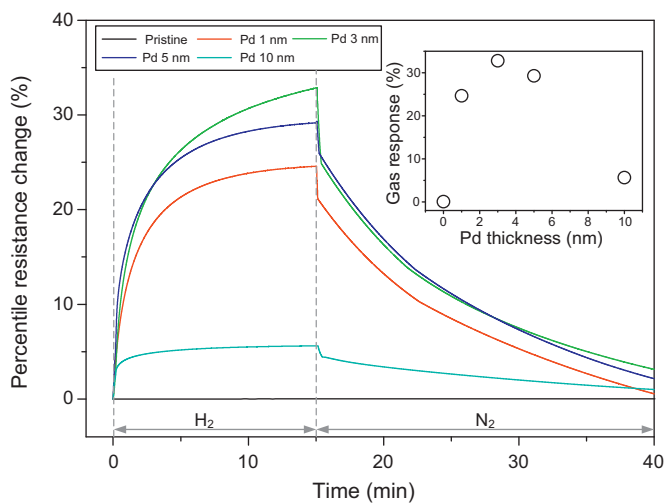

Fig. 3. The relative resistance changes of the graphene sensors exposed to 1000 ppm concentration of hydrogen gas. The gas responses of the sensors are plotted with respect to the Pd deposition thickness in the inset.

is determined by deposition thickness, improves a gas sensing performance, following investigations were carried out using the Pd–graphene sensor with a Pd thickness of 3 nm.

Fig. 4(a) presents the reproducible resistance change of the sensor when exposed to 1000 ppm hydrogen gas. During the repeated cycles of sensing the gas response slightly decreases and becomes saturated due to incomplete recovery characteristics of palladium hydride. The sensor recovery was relatively slow and incomplete in nitrogen gas flow. The recovery characteristics are closely related to the conversion of palladium hydride to palladium. The recovery could be improved by exposing the sensor to oxygen molecules which accelerate the recovery of hydrogen in palladium hydride by forming hydroxyl and water [12,20,21]. When the sensor operates in air by considering the recovery of the sensor, water vapor in the air is also dissociatively adsorbed on the Pd surface forming hydroxyl molecules with assistance of surface chemisorbed atomic oxygen [27]. We believe that once hydrogen gas is adsorbed as atomic hydrogen, a ready reaction between hydrogen and hydroxyl dominates the consumption of hydrogen gas into the formation of water, thereby reducing the formation of palladium hydride. It may decrease the sensing response of the sensor. Fig. 4(b) shows percentile resistance changes when exposed to different hydrogen

concentrations from 20 to 1000 ppm. The results were plotted as the relationship between the percentage of resistance change and time, which is useful to compare different devices with different initial resistance. The percentile resistance changes were calculated using the sensor resistance change normalized to the initial resistance at each sensing stage. The in situ measurement of the resistance change is also shown in the inset of the figure. The sensor exhibits a detectable signal ($\sim$1% in gas response) with low noise level at concentration as low as 20 ppm. The gas responses of the sensor are plotted with respect to the square root of hydrogen concentration, as shown in Fig. 4(c), which shows a linear correlation in accordance with the Langmuir adsorption isotherm theory. In the case of the dissociation of a molecule into two species (H_2 into $2H$), the process of adsorption is considered to be a reaction between the gas molecule and two surface sites [28]. At equilibrium (when the adsorption/desorption rates are equal), the relationship between the surface fraction occupied by adsorbates (Θ) and the pressure (P) or concentration of gas molecules is expressed as:

$$k_a \cdot P \cdot (1 - \Theta)^2 = k_d \cdot \Theta^2, \tag{2a}$$

or

$$\frac{\Theta}{1 - \Theta} = (K \cdot P)^{1/2} \tag{2b}$$

where the equilibrium constant (K) is defined by k_a/k_d, and k_a and k_d denote the adsorption/desorption rate constants, respectively. At low hydrogen concentration, the resistance change ($\Delta R/R_o \sim (K \cdot P)^{1/2}$) is in good agreement with our experimental result (Fig. 4(c)). The response time with respect to hydrogen concentration is shown in Fig. 4(d). The reciprocal of the response time which indicates the reaction rate shows a linear relationship with hydrogen concentration. At the initial stage of the measurement, the rate of hydrogen adsorption is $k_a \cdot P \cdot (1 - \Theta)^2$, where $(1 - \Theta)^2$ indicates the fraction of surface that is not covered by hydrogen. Since Θ is negligible at the initial stage, the adsorption rate is approximately $r \sim k_a \cdot P$. Therefore, the reciprocal of the response time corresponds to the initial hydrogen adsorption rate. As shown in Fig. 4(d), the hydrogen adsorption rate follows a linear relationship with hydrogen concentration, which indicates that the sensing kinetics of the sensor mainly relied on the hydrogen dissociation process over palladium.

Finally, bending tests were performed to evaluate the suitability of the sensor for flexible sensing application. Electromechanical properties of the sensor were tested as shown in Fig. 5(a). The normalized resistances of the sensor were plotted with respect to bending radius as described in the inset of Fig. 5(a). Fig. 5(b) shows the sensing responses exposed to 1000 ppm and 500 ppm hydrogen with respect to the bending radius of the sensor. The sensor does not show any significant degradation when it is bent to a curved geometry with a bending radius down to 3 mm.

In summary, we successfully fabricated the flexible hydrogen sensor using graphene decorated with Pd nanoparticles. The optimized graphene sensor with 3 nm-thick Pd exhibits a gas response of $\sim$33% when exposed to 1000 ppm H_2, and it is clearly detectable as low as 20 ppm H_2 at room temperature. The gas response becomes saturated during the repeated cycles of sensing and the
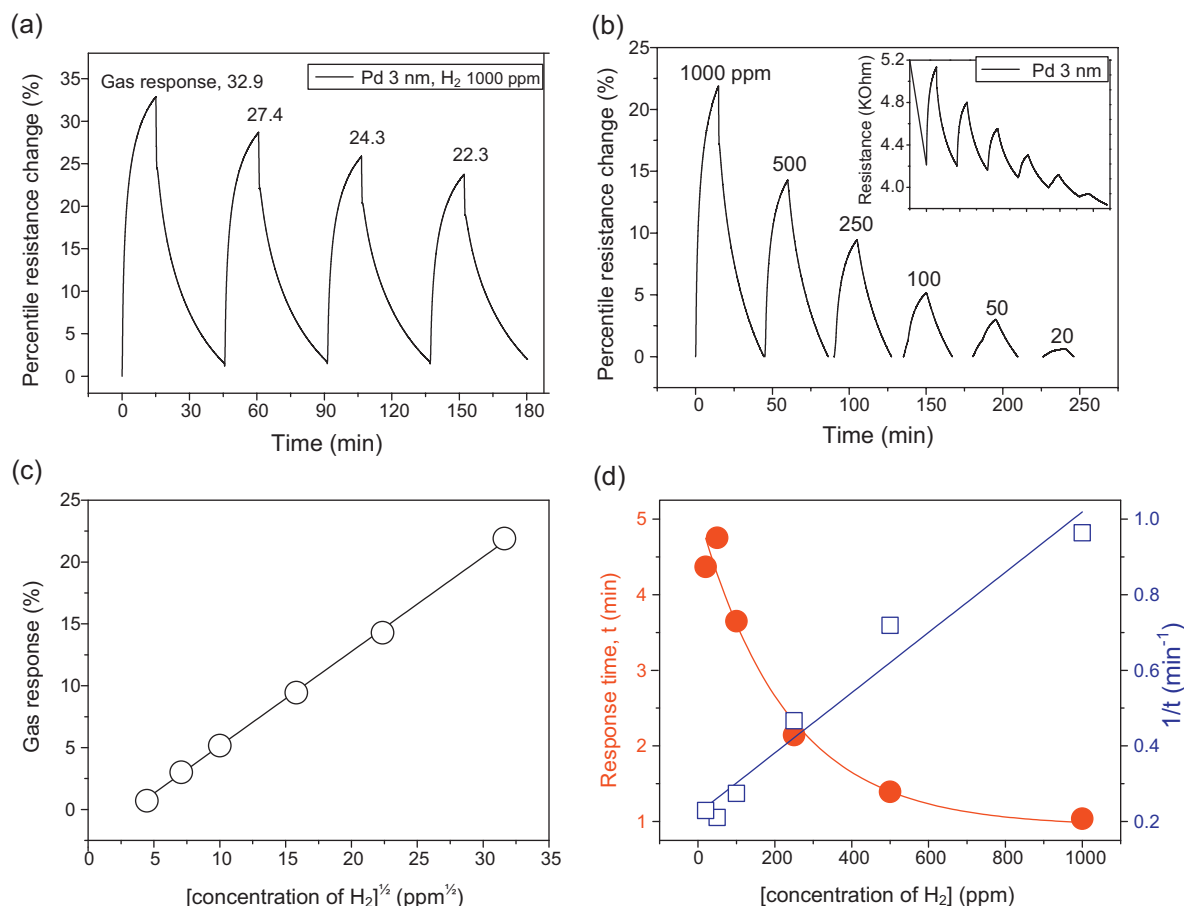

Fig. 4. Evaluation of sensing performance of the graphene sensor. (a) The reproducible resistance change of the sensor when exposed to 1000 ppm hydrogen gas. (b) The percentile resistance changes when exposed to different hydrogen concentrations from 20 to 1000 ppm. (c) The gas response with respect to the square root of hydrogen concentration. (d) The response time with respect to hydrogen concentration.
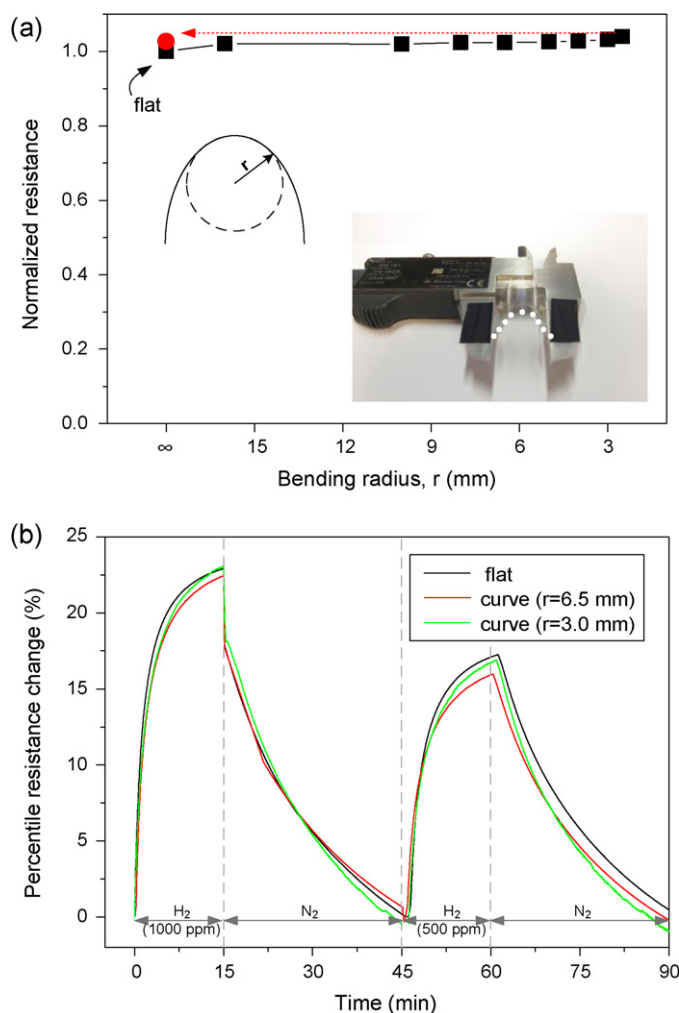
Fig. 5. Bending test for flexible sensing application. (a) The normalized resistance of the sensor with respect to bending radius. The red plot presents the normalized resistance when the sensor returned to the release state. (b) The sensing responses exposed to 1000 ppm and 500 ppm hydrogen with respect to the bending radius of the sensor. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sensor recovery was relatively slow. Incomplete recovery of palladium hydride may be responsible for the sensor responses in nitrogen carrier gas. The correlation between gas response and gas concentration was in good agreement with the Langmuir adsorption isotherm model. The suitability of the sensor for flexible sensing application was confirmed by mechanical bending tests, in which the sensor does not show any significant degradation when it is bent to a curved geometry with a bending radius down to 3 mm. The sensor performance could be improved by optimizing specimen preparation, such as patterning graphene having nano-size width and size/density control of palladium nanoparticles on graphene, is expected to yield significant performance improvement, especially in response time.

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