HIGH-PERFORMANCE HYDROGEN SENSOR BASED ON AN ARRAY OF SINGLE SUSPENDED CARBON NANOWIRES SELECTIVELY FUNCTIONALIZED WITH PALLADIUM NANOPARTICLES

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ABSTRACT

This paper reports a novel hydrogen sensor based on an array of single suspended carbon nanowires (Φ ~ 200 nm, length ~ 100 μm) decorated with various sizes (10 ~ 50 nm) of Pd nanoparticles; this H_2 sensor exhibits advantageous sensor performances such as room temperature sensing with high sensitivity, wide sensing range, and full recovery in 5 s via low power consumption (30 μW). These high performances are enabled by the novel architecture of suspended Pd nanoparticles/carbon nanowires facilitating enhanced mass transfer, high surface area to volume ratio, and good thermal insulation. This novel sensor platform can be fabricated using only simple batch microfabrication processes including carbon-MEMS that consisted UV-lithography and pyrolysis. The sensitivity and sensing range of the H_2 sensor can be modulated by controlling the size of Pd nanoparticles (10 – 30 nm Pd nanoparticles: 2.51%/ppm$^{1/2}$ and 10-7,000 ppm, 30 – 50 nm Pd nanoparticles: 0.36 %/ppm$^{1/2}$ and 10 ppm-5 %). Hence, wide range of H_2 sensing was enabled by integrating nanowires decorated with various Pd nanoparticles on a chip. Moreover, the gas response can be fully recovered in a very short time (e.g. 5 s for 1,000 ppm H_2) by self-heating at a carbon nanowire.

INTRODUCTION

H_2 gas which has been widely used in various industrial applications is explosive with a lower flammable limit of 4 % in air. Therefore, it is important to develop H_2 gas sensors with high sensitivity, fast response, and wide sensing range. Pd-based nanomaterials have been considered as a good candidate for the H_2 gas sensor material because of fast resistance change via H_2 absorption at room temperature. However, even with high sensitivity, However, Pd-nanomaterial based H_2 sensors showed narrow sensing range because of fast saturation even at low H_2 concentration. In addition to the fast saturation, the Pd-based H_2 sensor showed slow resistance recovery because of slow diffusion of hydrogen atoms at room temperature. This slow recovery can be a serious limitation in precise detection of H_2 of varying gas concentrations.

In this study, we have overcome two significant limitations in Pd-nanostructure-based H_2 sensors: narrow sensing range and slow resistance recovery. Wide sensing range is possible through fabricating an array of single carbon nanowires decorated with various size of Pd nanoparticles (Pd nanoparticles/carbon nanowire). For the fast resistance recovery of the sensor, Pd nanoparticles/ carbon nanowires is heated by applying additional current along the Pd nanoparticle/carbon nanowire (Self-heating). Owing to very limited heat loss because of the suspended long geometry of the PdNP/carbon nanowire, only 5 s heating with ultra-low power is enough for full resistance recovery. This fast fully gas response recovery enabled reproducible real-time H_2 gas sensing with long time periods without calibration.

EXPERIMENTAL

Fabrication

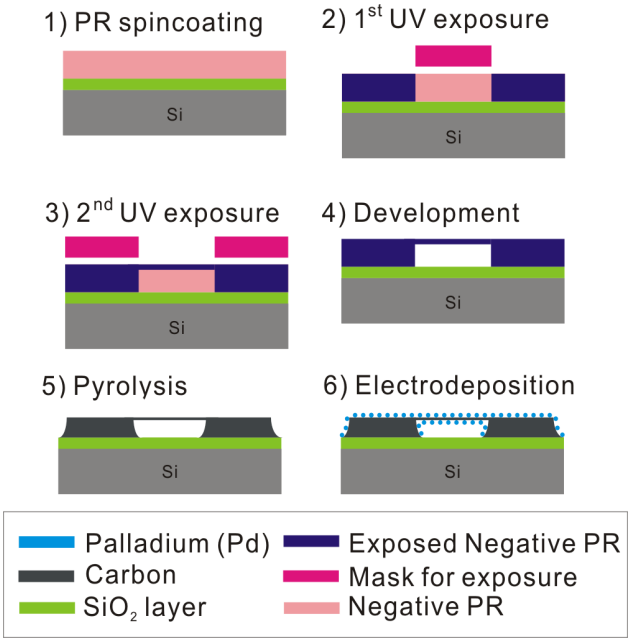


Figure 1: Schematic fabrication steps for a suspended Pd nanoparticles/carbon nanowire

An array of suspended carbon nanowires was fabricated using carbon-MEMS process consisting of UV-lithography and pyrolysis (Figure 1). Polymer microwires patterned by UV-lithography were converted into nano-sized carbon nanowires due to isotropic volume reduction in pyrolysis. On individual carbon nanowires, Pd nanoparticles were selectively integrated with different electrodeposition conditions (Type A: 1.0 V for 5 s after 1.5 V for 5 s; Type B: 1.5 V for 25 s after 1.0 V for 5 s).

Experimental set-up for H_2 sensor measurement

The gas responses of the PdNP/carbon nanowires were measured at atmospheric pressure in a chamber equipped with mass flow meters. Before H_2 gas detection, gas in the chamber was purged by several vacuum pumping and N_2 gas purging cycles. H_2 concentrations were controlled by mixing 0.1 % or 5 % H_2 in air and air using a gas flow controller (GMC1200, ATOVAC, Korea). While flowing the H_2/air gas mixture in the chamber, the electrical resistance change of the PdNP/carbon nanowires was measured using a source meter (Keithley 2450, Keithley Instruments, Inc., USA).

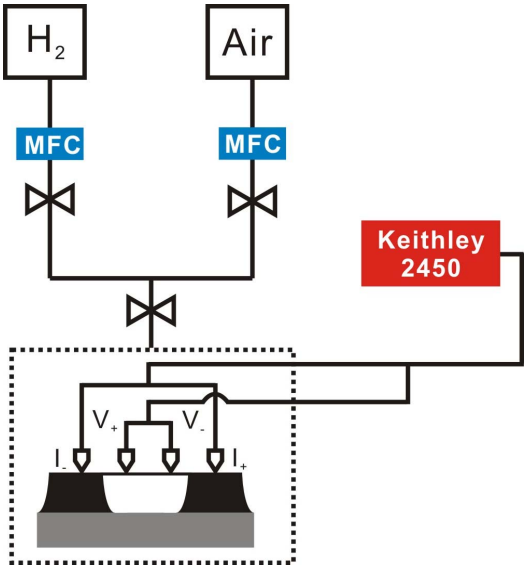


Figure 2: Experimental set-up including a gas chamber, mass flow controllers, and an analyzer system.

RESULTS

Morphologies of Pd nanoparticles

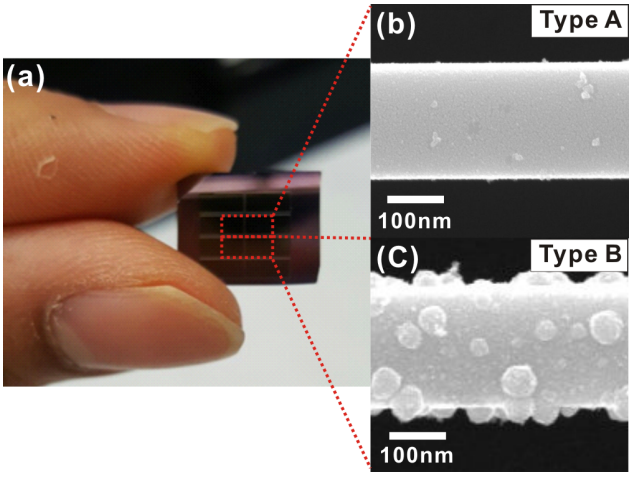


Figure 3: (a) A single chip integrated with an array of single suspended PdNP/carbon nanowires. SEM images of (b) small Pd nanoparticles (Type A) and (c) large Pd nanoparticles (Type B) integrated on suspended wires.

Two different sizes of Pd nanoparticles were deposited on single suspended carbon nanowires at a single chip. The two types of composite nanowires were named Type A and Type B depending on PdNP growth time. As the deposition time increases at the growth step from 5s to 25s, the sizes of PdNPs increase as shown in Figure 3. In this research, these two types of suspended PdNP/carbon nanowires, or Type A (nanoparticle size = 10 – 30 nm) and Type B (nanoparticle size = 30 – 50 nm) were utilized for the characterization of H_2 gas sensing performance.

Characteristics of PdNP/carbon nanowires

Electrical resistance of PdNP/carbon nanowire changes with the injection of H_2 gas because the resistance of Pd reduces via H_2 absorption into Pd lattice. The total electrical resistance along the PdNP/carbon nanowire is determined by resistances of the carbon core wire and the PdNPs. Therefore, the relative resistance of the carbon core to PdNPs should be high for the sensitive H_2 gas sensing. In this research, the electrical conductivity of the core carbon nanowire was modulated by controlling the pyrolysis temperature. Thus, the electrical resistance of the suspended composite nanowire was significantly reduced after PdNP deposition as shown in Figure 4.

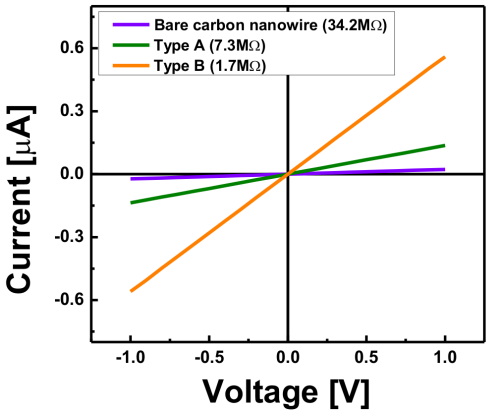
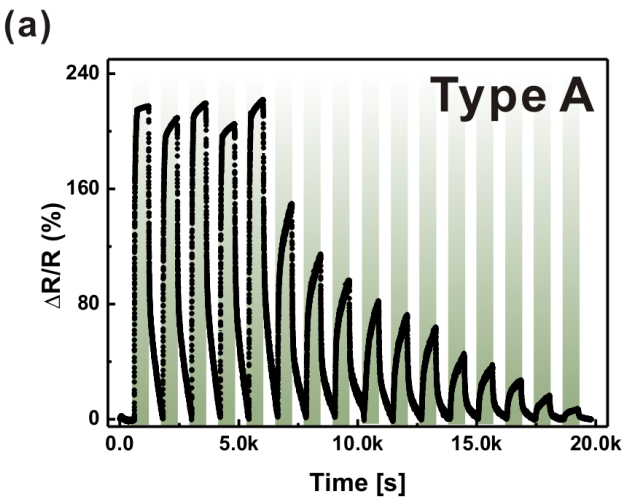


Figure 4: I-V characteristics of a suspended carbon nanowires before and after Pd nanoparticles deposition.

Real time H_2 gas sensing

Figure 5 shows the gas response (ΔR/R; R = resistance change before and after H_2 gas injection, R = resistance before H_2 gas injection) measurement results of PdNP/carbon nanowires of different types while varying the hydrogen concentration from 5 % to 10 ppm at room temperature. Type A with small PdNPs (10 – 30 nm) exhibits higher gas response (e.g. resistance change of 210% for 0.7% H_2 concentration) than that of Type B with large PdNPs (30 – 50nm) but its response stats to be saturated at 0.7 %. However, Type B exhibits continuous gas response increase up to 5 % of H_2.



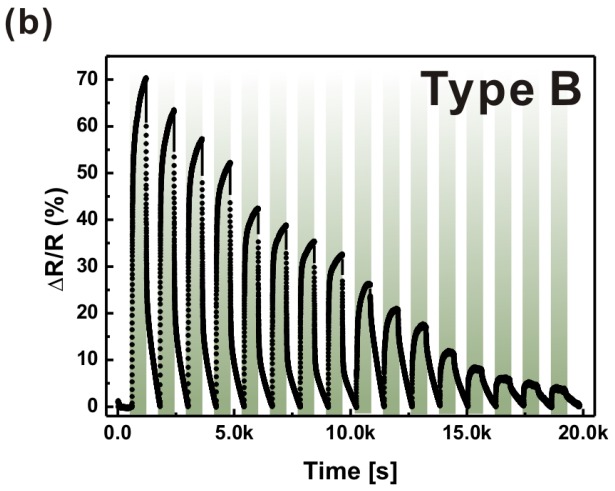


Figure 5: Gas responses of (a) Type A and (b) Type B suspended PdNP/carbon nanowires according to various H_2 concentrations (Green shade areas mean specific H_2 concentration environmenst; 5, 3.5, 2.5, 1, 0.7 and 0.3 % and 1000, 700, 500, 200, 100, 80, 50, 30, 20 and 10 ppm).

Self-heating effect

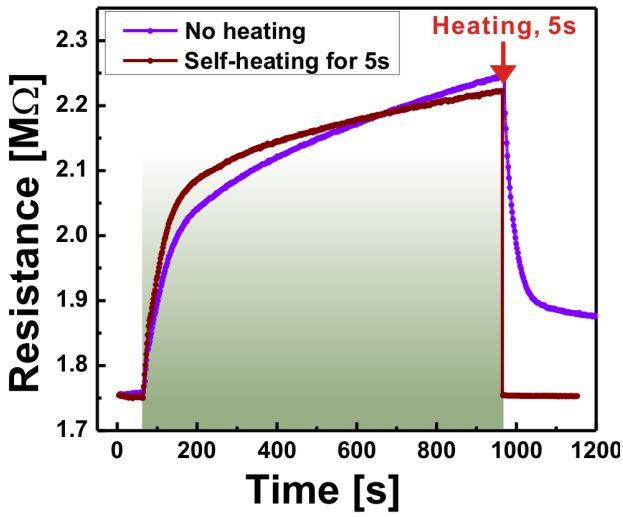


Figure 6: Gas response recovery behaviors of Type B composite nanowire at 1000 ppm H_2.

In order to enhance sensor signal recovery, a Type B PdNP/carbon nanowire was heated by Joule heating (30 μW) for 5 s just after H_2 gas was closed. Then, the wire resistance recovered instantaneously to its original value. This indicates the feasibility of the presented gas sensor as a precise real-time H_2 detection tool.

CONCLUSION

In this research, we developed a novel hydrogen sensor based on an array of single suspended carbon nanowires decorated with various sizes of Pd nanoparticles enabling room temperature H_2 gas sensing with high sensitivity, wide sensing range (10 ppm – 5 %). Also, the resistance was fully recovered in 5 s via low power consumption (30 μW). Our approach showed the great possibility to apply PdNP/carbon nanowires to real life with the advantages of fast recovery, wide sensing range, and low power consumption.

ACKNOWLEDGEMENTS

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