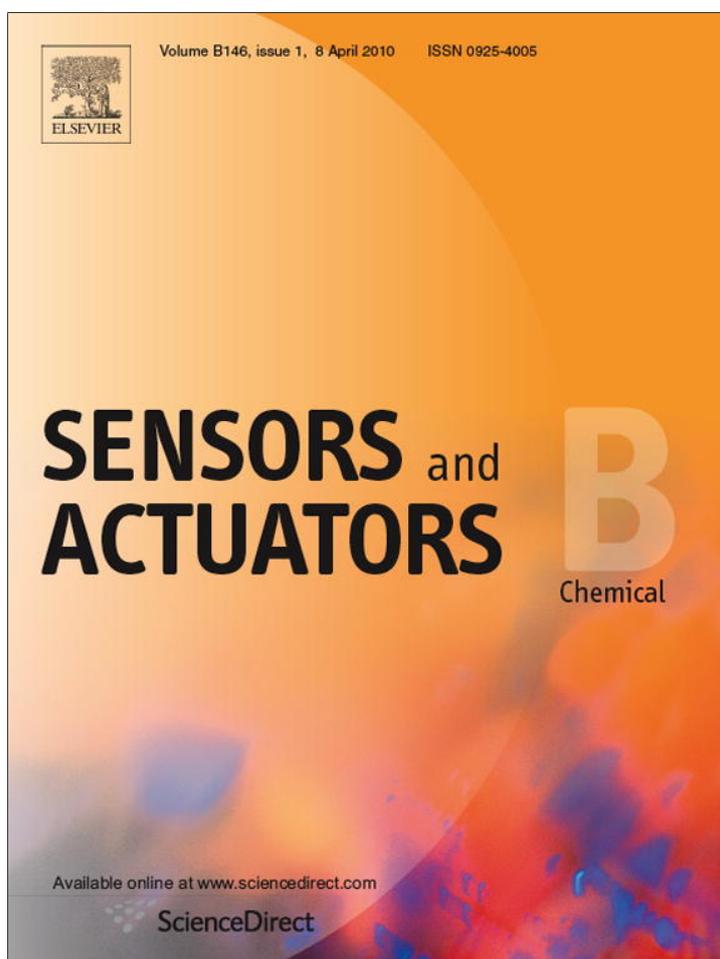


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Highly sensitive hydrogen gas sensors using single-walled carbon nanotubes grafted with Pd nanoparticles

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ABSTRACT

We have investigated the hydrogen gas sensing performance of single-walled carbon nanotubes (SWCNTs) grafted with Pd nanoparticles (NPs). The SWCNTs, modified with dendrimers before grafting, were found to have a much faster response time (3 s) and better recovery but lower response (8.6%) at 10,000 ppm hydrogen gas than those prepared without the dendrimer template (253 s, 25%). This can be ascribed to the dipole moments induced by the dendrimers. Removal of the dendrimers by heat treatment resulted in high response (25%), a fast response time (7 s) at 10,000 ppm hydrogen gas, and an ultra-low concentration H₂ detection of 10 ppm at room temperature. In addition, this sample was found to satisfy Sievert's law. Our results demonstrate that SWCNTs grafted with Pd-NPs through a dendrimer-mediated process can be used to fabricate highly sensitive hydrogen gas sensors that exhibit a broad dynamic detection range, fast response times, and excellent recovery.

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1. Introduction

Carbon nanotubes (CNTs) became an important research topic with the publication of the landmark paper by Iijima [1]. Having unique structures, excellent mechanical and electrical properties, and large surface area, CNTs are good candidates for a variety of applications. Recently, the combination of CNTs with metal nanoparticles (NPs) has attracted much attention, given the possibility of their use in electronics, as catalysts and as bio/chemical sensors [2–4].

In particular, research suggests that CNTs might be ideal materials for gas adsorption and detection because of their hollow centers, size, and large surface area [5]. Gas adsorption on CNTs is the focus of intense experimental and theoretical studies [6,7]. Considering that gas adsorption of CNTs modifies their electronic properties, Kong et al. [8] proposed the use of CNTs as gas sensors. However, CNTs are difficult to disperse in solution, hampering their practical use. Many scientists have attempted to chemically modify the surface of CNTs with various organic ligands or polymers to improve solubility. Dendrimers, a well-defined group of polymers,

have attracted considerable interest since 1985, when Tomalia et al. [9] first reported them as a new class of topological polymer of controllable size, structure, and functionalities. Dendrimers are characterized by three distinguishable properties: a core, an interior layer (repeating unit), and an exterior layer (terminal group). Their particular structure and functionality make dendrimers suitable as gene delivery agents or as protein/enzyme mimics. Also, metal NPs can be stabilized within dendrimers by encapsulation for catalytic applications. Pre-synthesized 3rd generation dendrimers have been attached to the surface of CNTs. Also, hyper-branched dendrimers have been synthesized directly on their surface. Sano et al. [10] synthesized star-shaped CNTs with a 10th generation polyamidoamine (PAMAM) dendrimers with amine. Sun et al. [11] modified CNTs with hydrophilic dendra that terminated with long alkyl chains [12,13].

Molecular sensing requires strong interaction between the sensor material and target molecules. In the case of hydrogen, however, pristine single-walled carbon nanotubes (SWCNTs) hardly interact with hydrogen gas [14]. Palladium (Pd), a catalyst with hydrogen gas sensing and hydrogen-storage capabilities, has been incorporated into CNTs to improve hydrogen gas response. A number of researchers have modified CNTs with Pd-NPs using chemical vapor deposition [11], sputtering [15], electron-beam evaporation or thermal evaporation [16,17], dielectrophoresis [18,19], and electrodeposition [20,21].

In a few reported cases, metal NPs were templated and stabilized on the surface of CNTs with the aid of dendrimers [22–26]. To our knowledge, the present paper is the first report of the fab-

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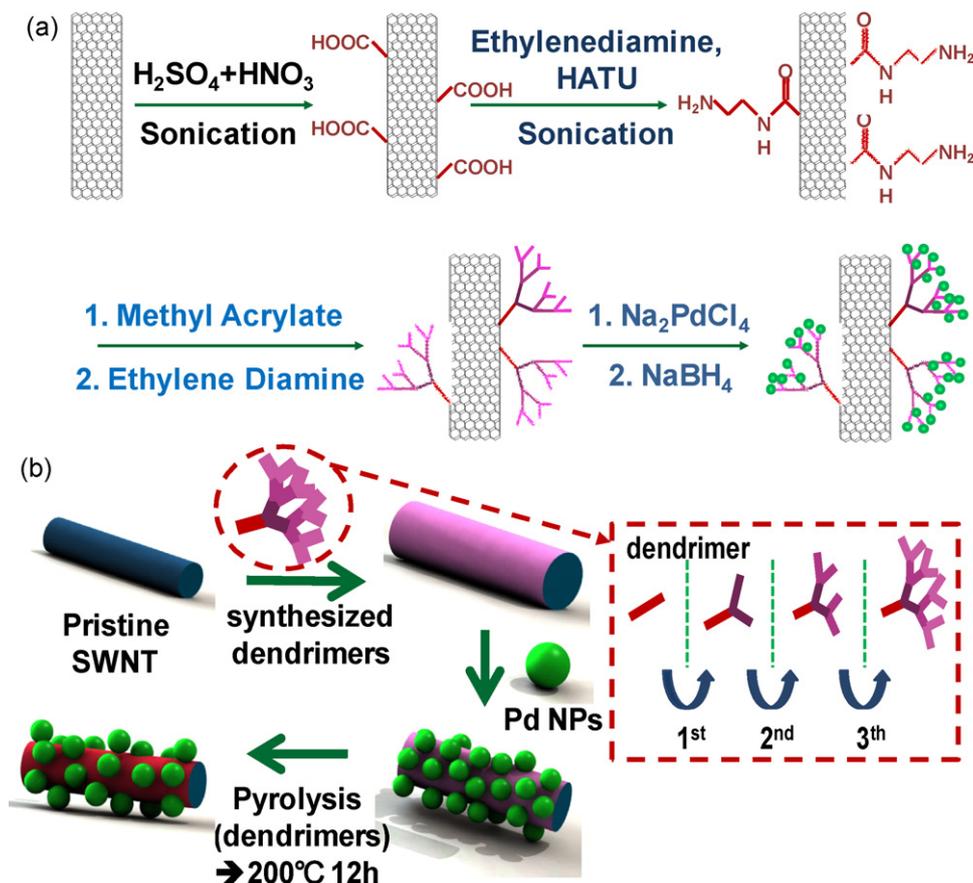


Fig. 1. The schematic illustrations of the modification of (a) SWCNTs with NH_2 -terminated PAMAM dendrimers and Pd-NPs, and (b) fabrication procedure for Sample III.

rication of hydrogen gas sensors from Pd-NP-grafted SWCNTs. The pyrolysis of the dendrimers enabled significant electrical conductance modulation when the assembly was exposed to extremely low concentrations (down to 10 ppm) of hydrogen gas in air. We discuss the effects of the dendrimers, including their pyrolysis of our SWCNT assembly.

2. Material and methods

2.1. Synthesis

SWCNTs (diameter: 1.0–1.2 nm; length: 20 μm ; purity: 60–70 wt%) were purchased from Iljin Nanotech (Seoul). The SWCNTs (20 mg) were treated with nitric acid (10 ml) and sulfuric acid (30 ml) and sonicated 3 h to form carboxyl groups on their surface (see Fig. 1(a)). The oxidized SWCNTs were reacted with ethylenediamine (20 ml) and N-[(dimethylamino)-1H-1,2,3-triazolo(4,5,6)pyridine-1-ylmethylmethanaminium hexafluorophosphate N-oxide] (hereafter refer HATU) and then sonicated 4 h to yield terminal amine groups [27]. The addition of hyper-branched PAMAM dendrimers to the surfaces of the SWCNTs was achieved by Michael addition (repeated twice) and amidation as described by Tomalia et al. [9]. Then Pd-NPs were grown on the surfaces of the dendrimer-modified SWCNTs in aqueous or acidic solution by reducing $0.1 \text{ M PdCl}_4^{2-}$ with 1.0 M NaBH_4 at $\text{pH} \approx 2$ (Sample II). Sample III was prepared by heating Sample II at 200°C under flowing Ar for 12 h to remove the dendrimers and then cooled back to 25°C (see Fig. 1(b)). For comparative study, Pd-NPs were grafted directly on SWCNTs (Sample I) without a dendrimer template.

2.2. Device fabrication

To fabricate devices based on the three types of sample sensors, Samples I, II, and III, a 20-nm thick Ti film and a 100-nm thick Au film were deposited on a thermally oxidized Si(100) substrate in an ultra-high vacuum direct current magnetron sputtering system with a base pressure of 4×10^{-8} Torr. A combination of photolithography and a lift-off process was used to fabricate micron-scale Ti/Au electrodes. Samples I, II, and III assemblies were dispersed on the Ti/Au electrodes on the substrate via micro-pipette drops and ultrasonic spreading of the nanotubes (see Fig. 2(a)). SEM, images of Sample III are presented in Fig. 2(b).

2.3. H_2 response measurements

The hydrogen gas sensing experimental setup consisted of a sealed chamber ($\sim 250 \text{ ml}$), mass flow controllers for monitoring the ratio of hydrogen gas to air, and digital multimeters connected to a personal computer. The gas chamber had a gas inlet and a gas outlet. The two gases were mixed from separate lines and flowed into the chamber through the gas inlet line of the chamber. The check valve opened at a pressure higher than atmospheric pressure. Thus, chamber pressure was held nearly constant at 1 atmosphere. The purity of the hydrogen gas was 99.9%. The real-time electrical resistance response to hydrogen gas was measured for Sample I, Sample II, and Sample III. Data was acquired with LabView software through a general-purpose interface bus interface card.

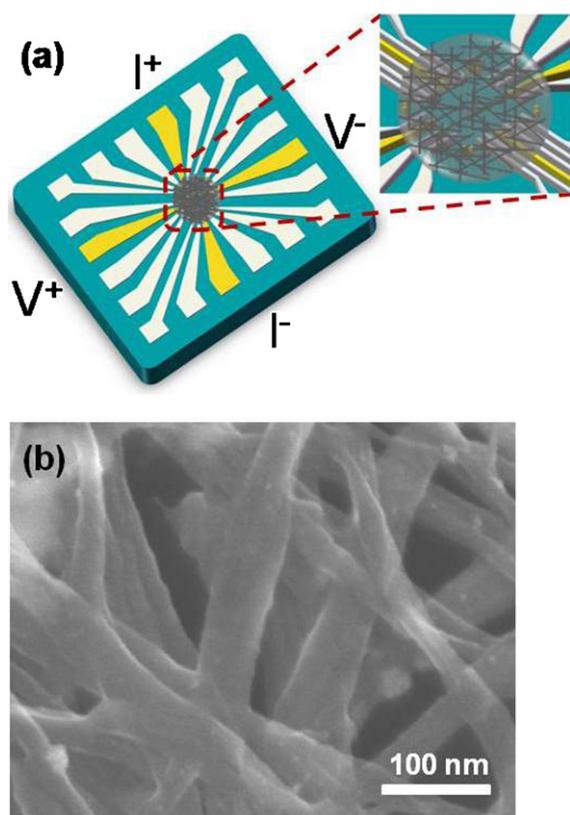


Fig. 2. (a) Schematic images of devices prepared by dispersing SWCNTs by micropipetting on Au electrodes on a substrate and (b) SEM images of Sample III.

3. Results and discussion

3.1. Compositional properties

We synthesized dendrimers on SWCNTs by reacting ethylenediamine and a coupling agent with the carboxylic groups on the surfaces of the SWCNTs via amide formation (see Fig. 1). The attachment of the dendrimers to the SWCNTs was confirmed by FT-IR spectroscopy. Similar results were reported previously in the literature [28]. The results of elemental analysis also confirmed the successful grafting of NH_2 -terminated PAMAM dendrimers on the SWCNTs. Nitrogen atoms were not observed in the pristine SWCNTs. When pristine SWCNTs were treated with sulfuric acid and nitric acid, a small amount of nitrogen atoms, 0.20 wt%, was detected from leftover nitric acid. In the reaction of ethylenediamine and HATU, there was direct coupling of ethylenediamine with the carboxylic groups on the surfaces of the SWCNTs. Elemental analysis showed that the nitrogen content increased greatly to 2.37 wt%. Further generation of PAMAM 1st to 3rd generation dendrimers on the SWCNTs resulted in a higher molar ratio of nitrogen: from 3.39 to 5.01 wt%. Such a result indicates that the number of amine groups attached to the surface of the SWCNTs increased continually during the sequential addition of dendrimers.

3.2. Raman spectroscopic studies

Raman spectroscopy revealed characteristic differences between the G bands for metallic and semiconducting CNTs. G bands comprise a G^- peak, which is associated with vibration along the circumferential direction of the SWCNTs, and a G^+ peak, which is attributed to vibrations along the CNT axis. In semiconducting

CNTs, the intensity of the G^+ peak is stronger than that of the G^- peak. In metallic CNTs, both the G^+ and G^- peaks are of equal intensity, but the G^- peak is much broader. In our samples, the G^- peak was observed at 1568 cm^{-1} and the G^+ peak at 1590 cm^{-1} . In Fig. 3, the intensity of the G^- peak is smaller than that of G^+ , and the G^- peak is very sharp. This means that the pristine SWCNTs are mainly semiconductors. The D band and the intensity of the peak observed at 1350 cm^{-1} in the Raman spectra are an indication of defects caused by the oxidation of the SWCNTs surfaces. The relative intensity ratio of the G band to the D band, I_G/I_D , of the pristine SWCNTs was 130.37. After oxidation of the SWCNTs, the I_G/I_D value decreased to 60.44; however, there were no further significant changes in the I_G/I_D values during subsequent dendrimer generation. Our data indicate that further generation of dendrimers does not affect the surface of the SWCNTs. Also, there was no significant change in the I_G/I_D value of Sample III obtained after treatment of Sample II, after pyrolysis of dendrimers.

3.3. HR-TEM and X-ray photoelectron spectroscopic studies

The Pd-NPs grown on the surface of Sample II in aqueous solution were uniform in size, with a diameter of 3.3 nm (see Fig. 4). The size distribution was estimated by measuring sizes of ~ 100 Pd particles from the TEM image (see Fig. 4(b)). However, when the pH of the PdCl_4^{2-} solution was adjusted to pH 2, the diameter of the Pd-NPs decreased to 2.4 ± 0.9 nm. Tomalia et al. suggested that since the tertiary amino groups were more basic than the primary amines, the nucleation of Pd-NPs likely occurred on the outer amine groups of the dendrimers in aqueous solution, whereas the nucleation of Pd-NPs probably occurred on the interior amino groups of dendrimers in acidic solution [29]. These results suggested that controlling the pH could control the size and location of Pd-NPs. Inductively coupled plasma-optical emission spectrometer analysis indicated that 12.09 wt% of Pd-NPs were functionalized in Sample III. X-ray photoelectron spectroscopy results showed the binding energy of palladium Pd^0 to be 335.4 ± 0.5 eV and 340.6 ± 0.5 eV.

3.4. H_2 response properties

We investigated the hydrogen gas sensing performance of Sample I, Sample II and Sample III. Fig. 5 shows high-resolution transmission electron microscopy, or HR-TEM, images (Fig. 5(a), (c), and (e)) and real-time electrical resistance responses (Fig. 5(b), (d), and (f)) to hydrogen gas for Sample I, Sample II, and Sample III respectively.

The density of Pd-NPs in Sample I was found to be very low. However, Sample II and Sample III were observed to have higher Pd-NPs densities than Sample I. The reason for this is the 3-dimensional structure of dendrimers, which act as hosts for Pd-NPs [30]. In other words, since the lone pair of electrons of the amine group can react easily with Pd cations, the addition of dendrimers with more amine groups stabilizes more Pd-NPs. Therefore, the dendrimers in Sample II and Sample III provide more Pd nucleation sites for Pd-NPs. There was no difference in the density of Pd-NPs in Sample II and Sample III. However, the particle size of Sample III was slightly larger than that of Sample II. We attribute this to the agglomeration of Pd-NPs after thermal annealing.

Representative electrical resistance ratios (R/R_0) to the presence of 10,000 ppm hydrogen gas at room temperature where the sensor resistance (R) has been normalized to initial resistance (R_0), which is the resistance in air for Sample I, Sample II, and Sample III are shown in Fig. 5(b), (d), and (f) respectively. The response (%) of the

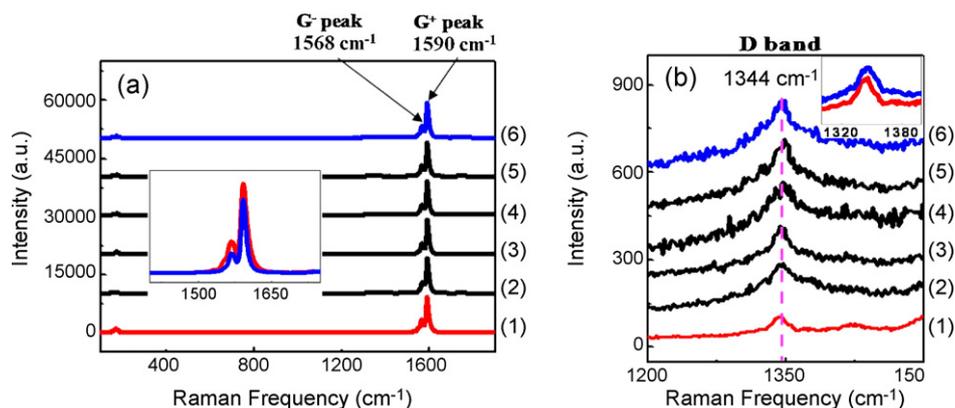


Fig. 3. Raman spectra of (a) G and (b) D band of (1) pristine SWCNTs, (2) oxidized SWCNTs, (3) NH₂-functionalized SWCNTs, (4) SWCNTs – 1st generation dendrimers, (5) SWCNTs – 2nd generation dendrimers, and (6) SWCNTs – 3rd generation dendrimers. G bands consist of a G⁻ (1568 cm⁻¹) and G⁺ (1590 cm⁻¹) peak.

samples is defined as:

$$\text{Response (\%)} = \frac{R_{\text{H}_2} - R_{\text{Air}}}{R_{\text{Air}}} \times 100,$$

where R_{H_2} and R_{Air} are the resistances in the presence of hydrogen gas and air respectively. Response time is defined as the time it takes to reach 36.8% ($=e^{-1}$) of the total change of the electric resistance at a given hydrogen gas concentration [31,32]. Fig. 5(b) shows the ratio in resistance of Sample I, exhibiting a response of 25% and a response time of 324 s. After Sample I was exposed to air, it did not return to the base line measurement indicating the importance Pd particles for carrier control. The response time of Sample II was 3 s, which was much faster than that of Sample I (324 s), as seen in Fig. 5(d). The response of Sample II, however, was found to be 8.6%, which was much lower than that of Sample I. The faster response time and lower response of Sample II can be explained by the attraction of dipole moments formed in SWCNTs with dendrimers 2–3 nm thick and Pd-NPs on the dendrimer ends [33,34]. Fig. 5(f) shows a response of 25% and a response time of 7 s at 10,000 ppm hydrogen gas for Sample III. The pyrolysis of Sample II at 200 °C plays a key role in reducing the distance between the SWCNTs and the Pd-NPs without a decrease in the number of the Pd-NPs [35] on the surface of the SWCNTs. Details on the mechanisms of Sample I, II, and III are described in the gas sensing mechanism section.

Fig. 6 displays (a) the real-time electrical resistance response to hydrogen gas for Sample III at various concentrations of hydrogen gas at room temperature, (b) variation of response with the

square root of hydrogen gas concentration, and (c) response time as a function of hydrogen gas concentration. Clear resistance changes were observed for various hydrogen gas concentrations in the range of 10–1000 ppm, as seen in Fig. 6(a). The inset of Fig. 6(a) shows a notable resistance change of 0.38% and a response time of 87 s, indicating that Sample III detected an ultra-low hydrogen gas concentration of 10 ppm. To the best of our knowledge, this is the lowest detection limit yet reported for CNT-based hydrogen gas sensors. At constant temperature, the following relationship between the outside hydrogen gas partial pressure P and the hydrogen gas concentration in a metal (H/Pd) exists:

$$\text{Response} \sim \frac{H}{\text{Pd}} = \left(\frac{1}{K_s} \right) P^{1/2}$$

This relationship is called Sievert's law, where K_s is Sievert's constant, which is temperature dependent, and H/Pd is the ratio of dissolved hydrogen atoms to the number of Pd-NPs. The correlation between response and hydrogen gas concentration (P) was found to be in good agreement with the law in the range of 10–1000 ppm (see Fig. 6(b)). From the fitted curve, the response at 10,000 ppm hydrogen gas is predicted to be 26%, which is consistent with the value (25%) obtained from our data, as shown in Fig. 5(f). Fig. 6(c) illustrates the variation in response time as a function of hydrogen gas concentration. Response time is inversely proportional to hydrogen gas concentration [36].

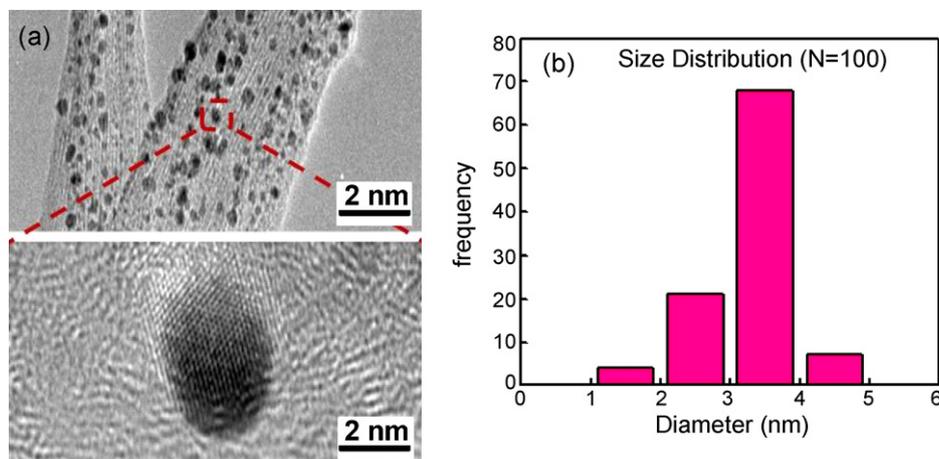


Fig. 4. (a) High-resolution TEM images of Sample II and (b) a histogram of the size distribution of Pd-NPs prepared in aqueous solution.

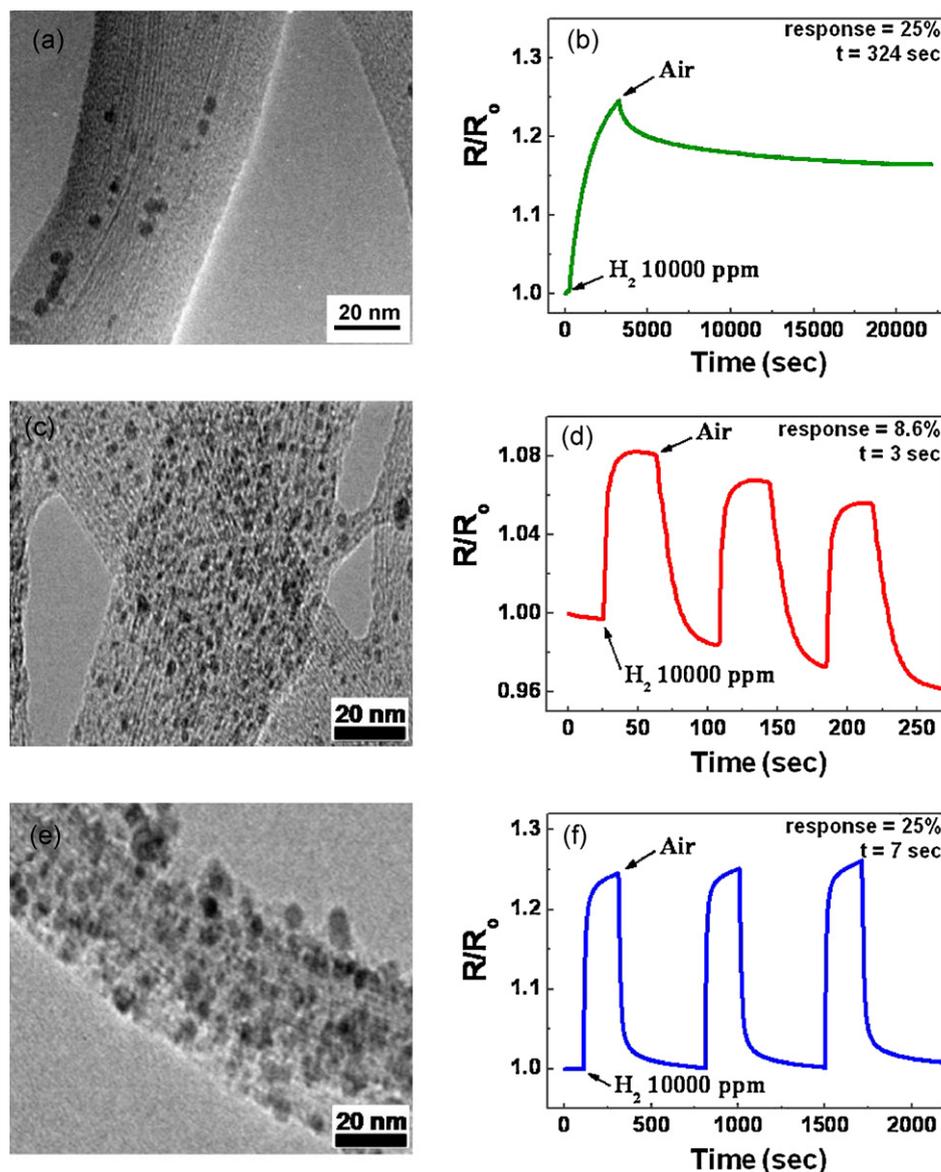


Fig. 5. High-resolution TEM images of (a) Sample I, (c) Sample II, and (e) Sample III. Representative electrical resistance responses to the presence of 10,000 ppm hydrogen gas at room temperature of (b) Sample I, (d) Sample II, and (f) Sample III.

3.5. H_2 sensing mechanism

We discuss the H_2 sensing mechanisms of the hydrogen gas sensors using single-walled carbon nanotubes grafted with Pd nanoparticles, which have high response, a fast response time and a low detection limit by comparing Pd-NPs-grafted directly on SWCNTs without a dendrimer template.

Pd-NPs-functionalized SWCNTs have been known to remarkably enhance the hydrogen gas detecting response of SWCNTs [14–16]. The fundamental mechanism of Sample I and III is the same commonly due to the interactions between H_2 , Pd, and SWCNTs, but number of Pd particles grafted on SWCNT is very low. Hydrogen molecules dissociate into atomic hydrogen on the surfaces of Pd-NPs at room temperature, dissolving into Pd with high solubility, and consequently lowering the work function of the Pd-NPs. The reduced Pd work function causes electron transfer from the Pd-NPs to the SWCNTs, which decreases hole-carriers for p -type transport, giving rise to increased electrical resistance [14].

In contrast with Sample I, Sample II showed enhanced H_2 sensing properties by attachment of the dendrimers to the SWCNTs.

After hydrogen atoms dissolve into the Pd-NPs, electron transfer is hindered by the dendrimers, but dipole moments are induced between the Pd-NPs and the SWCNTs. The formation of dipole moments is believed to account for the fast response time, since there is no need for the transfer of electrons across the junction barrier, which involves overcoming the activation energy. Our results demonstrate that the functionalized dendrimers on the SWCNTs improve the response time and reduce the response of a hydrogen gas detector because of the dendrimers on SWCNTs with formation of dipole moments and in spite of the increase in the density of the Pd-NPs.

To optimize the H_2 sensing properties of Sample II, removal of the dendrimers by heat treatment was performed without a decrease in the number of the Pd-NPs on the surface of the SWCNTs. The mechanism of Sample III implies that an increase in the amount of hole-carriers captured in the SWCNTs because of a decrease in the distance between the SWCNTs and the Pd-NPs gives rise to an increase in response to hydrogen gas. The dipole mechanisms can clearly explain the effects of dendrimers and heat treatment based on SWCNTs grafted with Pd nanoparticles as a hydrogen sensor in air.

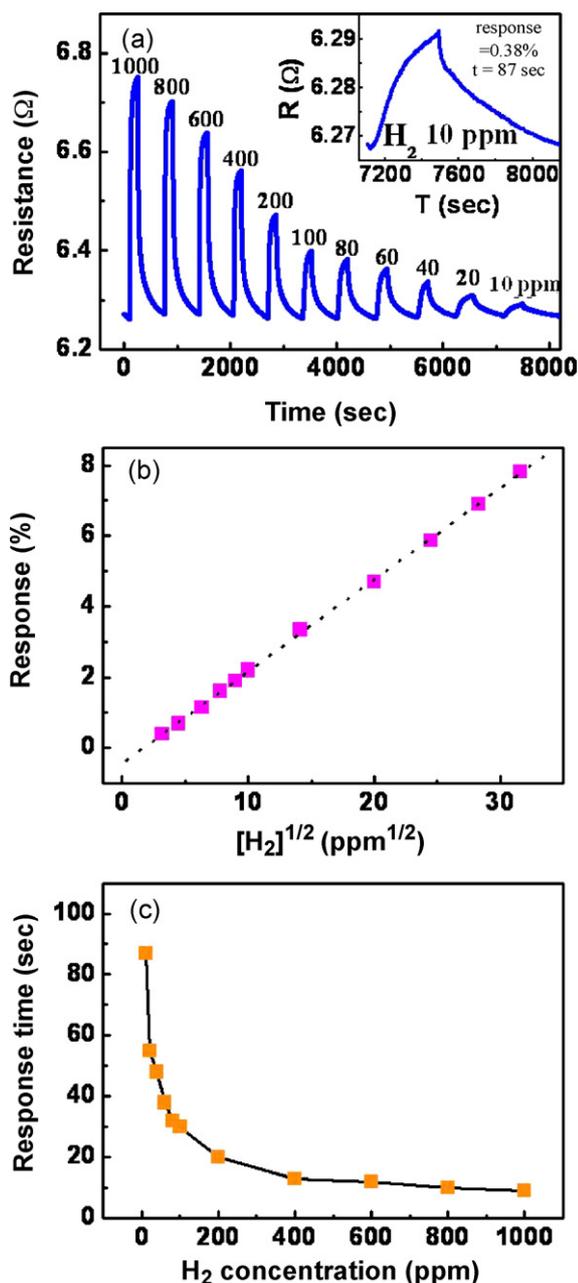


Fig. 6. (a) Real-time electrical resistance response of Sample III to hydrogen gas within a concentration range of 10–1,000 ppm at room temperature, (b) the variation of response with the square root of hydrogen gas concentration, and (c) the response time as a function of hydrogen gas concentration.

4. Conclusions

We successfully functionalized Pd nanoparticles (NPs) on the surfaces of single-walled carbon nanotubes (SWCNTs) by dendrimer-mediated synthesis using NH_2 -terminated PAMAM dendrimers. The size of the Pd-NPs can be controlled by adjusting the pH, and the number of attached Pd-NPs on the SWCNTs can be increased because of the presence of dendrimers on the SWCNTs. Pd-NPs-grafted directly on SWCNTs (Sample I) displayed a high response (25%) to hydrogen gas but a very slow response time (324 s) and poor recovery. Pd-dendrimer-SWCNTs (Sample II) showed good recovery and a much faster response time (3 s) but lower response (8.6%) than Sample I, which was attributed to induced dipole moments in the dendrimers. Sample III (fabri-

cated by heating Sample II) showed fast response time (7 s) and high response (25%), and satisfied Sievert's law, indicating that the pyrolysis of the dendrimers in Sample II played a key role in improving response by reducing the distance between the surface of the SWCNTs and the functionalized Pd-NPs. Our fabrication method allows the production of highly sensitive hydrogen gas sensors that exhibit a broad dynamic detection range, fast response times, and an ultra-low detection limit of 10 ppm.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2010.01.055.

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