

Fabrication of Pt-MWNT/Nafion Electrodes by Low-Temperature Decal Transfer Technique for Amperometric Hydrogen Detection

Muhammad Rashid¹, Tae-Sun Jun², and Yong Shin Kim^{1,2,*}

¹*Department of Applied Chemistry, Hanyang University, Ansan 426-791, South Korea*

²*Department of Bionano Engineering, Hanyang University, Ansan 426-791, South Korea*

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Abstract : A Pt nanoparticle-decorated multiwall carbon nanotube (Pt-MWNT) electrode was prepared on Nafion by a hot-pressing at relatively low temperature. This electrode exhibited an intricate entangled, nanoporous structure as a result of gathering highly anisotropic Pt-MWNTs. Individual Pt nanoparticles were confirmed to have a polycrystalline face-centered cubic structure with an average crystal size of around 3.5 nm. From the cyclic voltammograms for hydrogen redox reactions, the Pt-MWNT electrode was found to have a similar electrochemical behavior to polycrystalline Pt, and a specific electrochemical surface area of 2170 cm²mg⁻¹. Upon exposure to hydrogen analyte, the Pt-MWNT/Nafion electrode demonstrated a very high sensitivity of 3.60 μ A ppm⁻¹ and an excellent linear response over the concentration range of 100-1000 ppm. Moreover, this electrode was also evaluated in terms of response and recovery times, reproducibility, and long-term stability. Obtained results revealed good sensing performance in hydrogen detection.

Keywords : Hydrogen sensor; Electrochemical gas sensor; Pt-MWNT electrode; Hot-pressing

1. Introduction

Amperometric hydrogen gas sensors based on solid polymer electrolyte have received a large amount of attention due to their particular merits.¹⁻³⁾ Compared with other hydrogen sensors using different detection principles, they can operate at ambient temperature and provide a linear response with high sensitivity and selectivity. The use of solid polymer electrolyte can solve the problems of leakage, corrosion, and volatilization in liquid electrolyte sensors, and achieve a miniaturized electrochemical sensor with small size and light weight. Nafion (Dupont, USA), one polymer electrolyte membrane, has been widely used in the development of fuel cells and electrochemical gas sensors. It owns an excellent ionic conductivity, a good permselectivity, an outstanding chemical and thermal stability and a good mechanical strength.⁴⁻⁶⁾

Many attempts have been made to develop a Pt/Nafion electrode as the key component in amperometric hydrogen sensors since Pt metal has an excellent electrocatalytic activity for hydrogen oxidation and both Pt and Nafion are chemically inert. Various deposition techniques were established to platinize the Nafion surface, including mechanically pressing,⁷⁾ vacuum sputtering,⁸⁾ electrochemical deposition,⁹⁾ and chemical deposition based on a Takenaka-Torikai method^{10,11)} and an impregnation-reduction technique.¹²⁻¹⁵⁾

For achieving good sensing performance in the Pt electrode system, it is necessary to maximize and maintain a surface area of Pt catalysis. In order to fulfill this requirement efficiently, the sensing electrode can be prepared via stable anchoring of many small-sized Pt nanoparticles (NPs) on porous supporting materials as in various catalysis applications. Carbon nanomaterials such as carbon black, carbon nanofiber, carbon nanotube, and graphene have been widely used as the supporting matrix. Among them, multiwall carbon nanotubes (MWNTs) have attracted

*E-mail: yongshin@hanyang.ac.kr

great interest as the matrix material due to their unique one-dimensional nanostructures, high electrical conductivity, excellent chemical stability and low cost. Recently, Pt NP-decorated MWNT (Pt-MWNT) electrodes reported promising electrocatalytic activity for the ethanol or methanol oxidation^{16,17)} and non-enzymatic glucose sensing.¹⁸⁻²⁰⁾ In our previous work, a Pt-MWNT electrode was successfully formed on a porous polytetrafluoroethylene (PTFE) membrane through the filtration method, and was proved to have good electro-catalytic activity in hydrogen detection.²¹⁾

This paper presents an amperometric solid polymer electrolyte hydrogen sensor using a new Pt-MWNT/Nafion electrode prepared by hot-pressing a Pt-MWNT layer onto one side of Nafion. Material properties of the Pt-MWNT composite layer were characterized by various material analysis methods such as SEM, TEM, EDS and XRD. Cyclic voltammetry and chronoamperometry were employed to evaluate its electrochemical behavior and H₂-sensing performance including sensitivity, response and recovery times, reproducibility, and long-term stability. The relationship between the material properties of the Pt-MWNT electrode and its H₂-sensing performance are investigated and discussed.

2. Experimental

2.1. Preparation of Pt-MWNT/Nafion electrode

A circular piece of Nafion-117 membrane (Du Pont, diameter = 24 mm) was pretreated to prepare an impurity-free, protonated form (H⁺-Nafion). It was first washed in a de-ionized (DI) water bath at 85°C, and then cleaned in a 5% H₂O₂ aqueous solution at 75°C for 1 h. After rinsing with DI water, it was dipped in 0.5 M H₂SO₄ at 75°C for 1 h and then kept in boiling DI water for 1 h. The prepared membrane was stored in DI water to maintain the hydrated H⁺-Nafion state before a use.

Purified MWNTs (Iljin Nanotech, grown by CVD, purity >95%) were used without further purification. The 100 mg MWNTs were oxidatively activated by vigorous refluxing in 30 mL concentrated nitric acid for 6 h. Oxidized MWNTs were filtered and washed several times with DI water to remove residual HNO₃ and impurities. The filtered sample was dried overnight at 100°C in ambient air. Afterward, 2 mg

of the activated MWNTs were homogeneously suspended in 100 mL ethanol with the aid of 2 mg sodium dodecylsulfate (SDS) surfactant under ultrasonic agitation for 6 h. Then, 0.4 mL of a 250 mM NaBH₄ solution was added to the 19.4 mL MWNT dispersion. To initiate the formation of Pt NPs, 0.2 mL of a 100 mM H₂PtCl₆ solution was added dropwise into the mixture solution over a period of 15-20 min under stirring. The reaction solution was continuously stirred for 1 h for the complete reduction of Pt salts. Fig. 1 displays a schematic fabrication process diagram for the Pt-MWNT/Nafion electrode. After ultrasonic agitation for 1 h, the Pt-MWNT solution was filtered via vacuum-controlled aspiration onto a micro-porous PTFE membrane (PM28Y, Porex), and was washed several times with DI water in order to eliminate impurities such as Na⁺, Cl⁻, SDS and unreacted reactants. A circular Pt-MWNT/PTFE electrode with a 20 mm diameter was dried at a temperature of 90°C for 1 h in a vacuum oven. An additional ionomer thin-film, acting as an adhesion layer, was formed by coating a 5wt% Nafion solution (Aldrich) on the Pt-MWNT surface.²²⁾ This multi-layered decal substrate (ionomer/Pt-MWNT/PTFE) was pressed on the pretreated Nafion membrane at 45 kgf cm⁻² pressure and 90°C to prepare the Pt-MWNT/Nafion electrode.

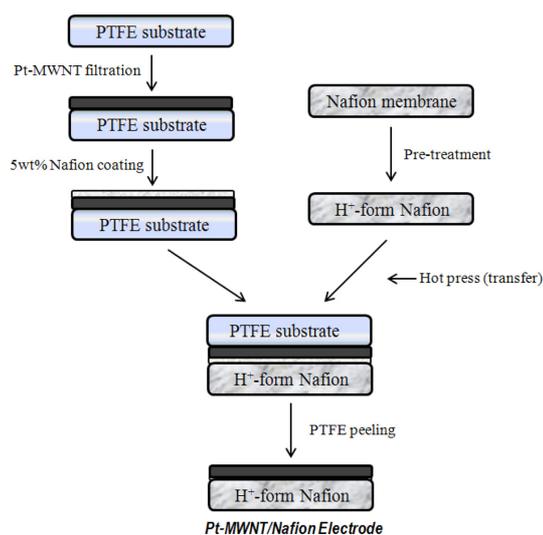


Fig. 1. A schematic process diagram for the fabrication of the Pt-MWNT/Nafion electrode using the hot-pressing method.

2.2. Material characterizations

Surface morphologies of the Pt-MWNT samples were inspected by scanning electron microscopy (SEM; S-4800, Hitachi). Transmission electron microscopy (TEM; JEM-2100F, JEOL) was carried out in order to investigate detailed nanostructures. TEM samples were prepared by dropping a small amount of a well-dispersed Pt-MWNT solution onto a carbon-coated copper grid. Elemental compositions were probed via energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD) patterns were also measured by an X-ray diffractometer (D/Max-2500, Rigaku) with a Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) source operated at 40 kV in order to confirm crystalline structures. Thickness and sheet resistivity were measured by a digital micrometer (ID-C112XBS, Mitutoyo) and a four point probe (RS 8, Dasol Eng.), respectively. Pt loading of the Pt-MWNT electrode was determined by the gravimetric method. The weighting was carried out by using a microbalance (BM-22, AND) just after drying a sample in a vacuum oven.

2.3. Electrochemical and gas-sensing measurements

Cyclic voltammograms (CVs) were measured using an electrochemical analyzer (Model 624C, CHI) under the three-electrode configuration at ambient temperature. A mercury sulfate electrode (Hg/Hg₂SO₄, saturated K₂SO₄) and a Pt wire were used as a reference and a counter electrode, respectively. A working electrode was prepared by dispensing a 60 mL Pt-MWNT solution containing 11.7 mg Pt on a commercial glassy carbon disk electrode. The measurements were carried out in 0.5 M H₂SO₄ aqueous solution at the scan rate of 10-100 mV s⁻¹ in the potential range of 0.0-1.4 V vs. a normal hydrogen electrode (NHE). Before the CV measurements, the electrolyte solution was purged with N₂ gas for 30 min to remove O₂ molecules dissolved in the solution. A stable and reproducible CV was observed after several successive scans. The specific electrochemical surface area (ESA) of the Pt-MWNT electrode was calculated by the relationship:

$$ESA = \frac{Q_H}{mq_m} \quad (1)$$

where Q_H is the hydrogen adsorption/desorption charge calculated from the CV curve measured at

20 mV s⁻¹, m is the weight of Pt loading, and q_m is the ideal charge density for the perfect formation of atomic hydrogen monolayer with a unit area. The q_m value was reported to be 210 mC cm⁻² for a polycrystalline Pt surface.²³⁾

All gas-sensing measurements were also performed using a CHI 624C electrochemical analyzer at room temperature. One PTFE sheet (PM28Y, Porex) was positioned in front of the Pt-MWNT/Nafion working electrode to act as a diffusion barrier layer for gaseous analytes. The PTFE/Pt-MWNT/Nafion membrane functioned as a separator to divide the electrochemical cell into gas and liquid compartments. The liquid chamber was filled with a 1.0 M H₂SO₄ solution, and a Pt wire was placed in the solution to serve as a counter electrode. A saturated calomel electrode was used as the reference. Amperometric sensing responses were measured at a polarization potential of 0.34 V vs. NHE upon exposure to the target H₂, CO and NH₃ gases. The analyte concentrations were regulated by changing the relative ratio of a sample flow rate to a N₂ carrier flow. The sample flow was generated from gas cylinders with the analytes of a fixed concentration. The flow rates were controlled by mass flow controllers, and the total flow rate was maintained to be 100 sccm.

3. Results and Discussion

3.1. Material properties of Pt-MWNT

A uniform Pt-MWNT composite film was formed on PTFE by filtering the 20 mL Pt-MWNT solution containing 20 mmol H₂PtCl₆ and 0.32 mg MWNT. Fig. 2(A) shows a surface SEM image of the Pt-MWNT sample. It exhibited an intricate entangled and porous structure resulting from the one-dimensional MWNTs as reported previously.²¹⁾ In addition, there were a great number of spherical Pt aggregates with sizes of around 45 nm on the MWNT surface. The microstructural features of the Pt NP-decorated MWNT were inspected in detail by TEM analysis, as shown in Fig. 2(B). The image clearly demonstrated that dark Pt NP clusters were well attached on the sidewall of the MWNT and the individual Pt particle size was in the range of 1.0-5.0 nm. This observation strongly supported

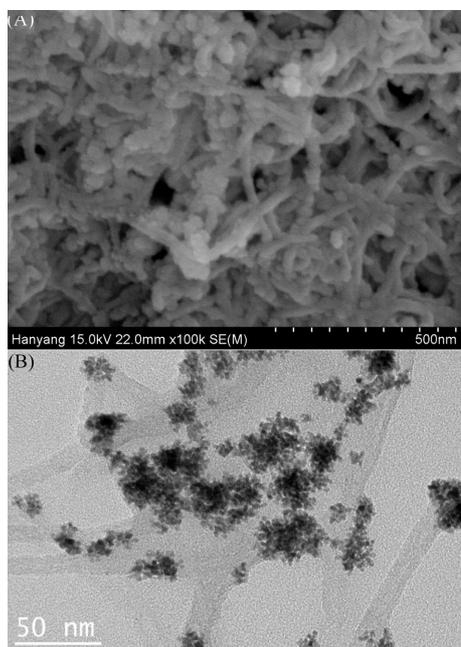


Fig. 2. (A) Surface SEM image of the Pt-MWNT film prepared on Nafion membrane. (B) TEM image of the Pt-MWNT nanocomposites.

the heterogeneous nucleation and growth of Pt NPs on the MWNT surface. The oxygenated chemical functional groups (-COOH, -CO-, -OH, etc.) formed after the acid treatment acted as nucleation sites and activated positions for the anchoring of Pt NPs due to their hydrophilic nature and high chemical activities.²⁴⁾ Furthermore, the interwoven structure of Pt NP-decorated MWNT nanocomposites was observed to be maintained after the layer was transferred onto a Nafion substrate by the hot-pressing. Atomic compositions of the transferred Pt-MWNT were confirmed by EDS, indicating the presence of carbon and platinum atoms. Their relative atomic number ratio was C : Pt = 87 : 13. No other elements were recognizably detected in the EDS spectrum, which implied that impurity contamination was negligible during the wet synthesis step and hot-pressing process.

A XRD pattern of the Pt-MWNT composites were measured, and was well assigned to the crystal planes of the face-centered cubic Pt crystal with a lattice constant of $a = 3.92 \text{ \AA}$ (JCPDS card No. 04-0802). This result indicated the successful forma-

tion of crystalline Pt particles. Moreover, the broad nature of the peaks implies that the Pt crystals were very small. The average Pt crystal size of the most intense Pt (111) peak was calculated to be 3.3 nm by the Debye-Scherrer equation, which was well consistent with the crystal size observed in the TEM image.

Consequently, working electrodes consisting of Pt NP-decorated MWNTs were successfully fabricated on a Nafion polymer electrolyte membrane by using the wet chemical synthesis, vacuum filtration, and hot-pressing processes. Since the resultant Pt-MWNT layer had structural characteristics of a high porosity and small-sized Pt NP-anchored MWNTs, this electrode would become a promising candidate for a gas diffusion working electrode in amperometric hydrogen sensors.

3.2. Electrochemical properties of Pt-MWNT electrode

Figure 3 shows CV curves of the Pt-MWNT electrode, measured at six different scan rates of 10, 20, 40, 60, 80 and 100 mV s^{-1} , for the hydrogen redox reactions in 0.5 M H_2SO_4 . The broad peak at a potential above 0.75 V in the positive scan was interpreted as the oxide formation on the Pt surface while the corresponding oxide reduction was observed in the negative scan with a peak located in the region of 0.5-0.67 V. In addition, there were two distinct peaks

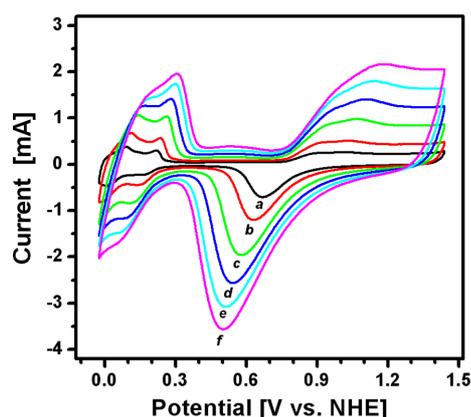


Fig. 3. CV curves of the Pt-MWNT/Nafion electrode in 0.5 M H_2SO_4 at different scan rates of a) 10, b) 20, c) 40, d) 60, e) 80, and f) 100 mV s^{-1} . As the scan rate increases, the looped CV curve expands outside. The potential is referenced to the normal hydrogen electrode (NHE).

for hydrogen adsorption and desorption processes each in the potential window of 0.0-0.3 V. The adsorption peaks were observed at 0.01 and 0.16 V for the innermost CV (scan rate = 10 mV s^{-1}) while the desorption peaks appeared at 0.09 and 0.22 V. The appearance of multiple peaks has been reported in polycrystalline Pt electrodes since different crystalline Pt planes led to adsorption and desorption sites with different force interactions between hydrogen and the Pt surface.²⁵⁻²⁷⁾ The stronger the interaction was, the more positive its redox potential became. Cathodic and anodic peaks observed at 0.16 and 0.22 V correspond to hydrogen adsorption and desorption at strongly-bonded sites, respectively. The formal potential E^0 for the strong adsorption/desorption site was calculated to be 0.19 V through by averaging cathodic and anodic peak potentials: $E^0 = 1/2(E_{pc} + E_{pa})$. This potential was consistent with the previously reported value in pure Pt electrodes.¹⁵⁾ Cathodic and anodic plots of peak current i_p vs. square root of scan rate $v^{1/2}$ for the strongly-chemisorbed hydrogen yielded very straight lines having a correlation coefficient higher than 0.999 in the linear regression analysis. The anodic and cathodic peak currents were comparable in magnitude. These results suggested that the hydrogen redox reactions on the planar Pt-MWNT electrode exhibited a quasi-reversible behavior. Consequently, these CV results imply that our Pt-MWNT electrode has a high electrochemical activity for the hydrogen redox reactions and its electrochemical characteristics were predominantly affected by the small-sized polycrystalline Pt NPs.

The ESA of the Pt-MWNT electrode was calculated to be $2170 \text{ cm}^2 \text{ mg}^{-1}$ from the charges collected in the hydrogen adsorption and desorption regions after the double-layer correction. This ESA of MWNT-supported Pt nanoparticles was much larger than the ESA values of $30\text{-}140 \text{ cm}^2 \text{ mg}^{-1}$ in the Pt film electrodes prepared by the chemical reduction methods.²⁸⁾ The ESA value is summarized in Table 1 together with other material properties of the Pt-MWNT sensing electrode used in the H_2 -sensing experiments, including a Pt loading, thickness and sheet resistance.

3.3. Amperometric hydrogen detection

Current-potential curves of the Pt-MWNT/Nafion electrode were measured for the oxidation of 1000 ppm hydrogen under different polarization

potentials in order to optimize a bias voltage. The applied potential was increased sequentially from 0.04 to 0.74 V. As the potential increased, the response current rapidly increased and then reached a plateau in the potential region of 0.24-0.54 V. The response current depends both on kinetics of hydrogen oxidation on an electrode surface reactions and hydrogen transfer efficiency to the electrode at the same concentration. Since the oxidation rate becomes faster at higher overpotential, the plateau behavior suggests the achievement of a mass transfer-limited condition for hydrogen oxidation on the Pt-MWNT electrode. Thus, all gas-sensing experiments were performed at a polarization potential of 0.34 V vs. NHE in this work.

A typical amperometric response curve of the Pt-MWNT/Nafion electrode is shown in Fig. 4 when hydrogen analyte is sequentially supplied with increasing the concentration in the range of 100 to 1000 ppm with a step of 100 ppm. The response current promptly increased and approached to a steady state during the detection time of 3 min, and then returned to its initial level within the following 5 min recovery period. The steady state responses in anodic current exhibited a linear increase in magnitude with increasing H_2 concentration. The inset displays a plot of response current vs. H_2 concentration. Response current variation was well represented by a linear line: $I_{res}(\mu\text{A}) = 3.60$

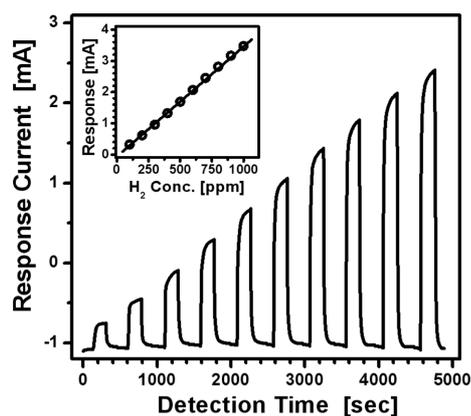


Fig. 4. An amperometric response curve of the Pt-MWNT/Nafion sensor for gradually increasing concentration of hydrogen in the range of 100-1000 ppm. The inset displays a variation of the anodic response current as a function of hydrogen concentration.

$\times C_{H_2}(ppm) - 88.0$. The correlation coefficient in the linear regression analysis was 0.9997, illustrating an excellent linear relationship between H_2 concentration and amperometric response over the concentration range of 100-1000 ppm. Gas-sensing sensitivity in amperometric sensors is commonly defined as a slope of the linear response line. The H_2 detection sensitivity of our Pt-MWNT/Nafion electrode (area = 3.14 cm^2) corresponded to $3.60 \mu\text{A ppm}^{-1}$. This sensitivity has been much higher than the previous values obtained at various sensing electrodes for amperometric H_2 detection: $0.152 \mu\text{A cm}^{-2} \text{ ppm}^{-1}$ for the Pt/Nafion electrode, $0.716 \mu\text{A ppm}^{-1}$ for the Pt-C/Nafion electrode, and $2.48 \mu\text{A ppm}^{-1}$ for the Pd/Nafion electrode (see Table 1 of Ref.¹¹). Furthermore, the Pt loading of 1.0 mg cm^{-2} was several times less than the optimum Pt loadings of previously reported solid polymer electrolyte H_2 sensors: 5.2 mg cm^{-2} for the Pt electrode,¹⁰ and 3.0 mg cm^{-2} for the Pt-C electrode.²⁹ Therefore, the well-dispersed and nano-sized Pt NP-decorated MWNT sensing layer provided the opportunity to fabricate a sensitive H_2 sensor with a small amount of Pt. In addition, the background noise in the response current, determined by the standard deviation of residuals about the average value of the baseline current, was evaluated to be $2.34 \mu\text{A}$. If the limit of detection (LOD) is defined as the concentration at which a sensor response has three times the noise level ($S/N=3$), the LOD is estimated to be about 2.0 ppm.

The linear relationship between the response current and the concentration could be interpreted with one of two limiting conditions: surface electron transfer reaction-limited or analyte diffusion-limited detection. Judging from the polarization curve mentioned above, the current response of the gas-diffusion PTFE/Pt-MWNT/Nafion electrode would be limited by the diffusion rate of H_2 into the sensing electrode. In this limit, the response current I_{res} was expressed by the following equation:

$$I_{res} = \frac{2qAD_{H_2}}{d} [H_2]_{gas} \quad (2)$$

where q , A , D_{H_2} , $[H_2]_{gas}$ and d are the electrical charge of an electron, the surface area of the diffusion barrier, the diffusion coefficient of H_2 , the H_2 concentration in the gas phase, and the thickness of the barrier layer, respectively. The response current would be directly proportional to the H_2 concentration under the conditions of having constant values for the other parameters. The linear relationship observed in Fig. 4 demonstrated that the Pt-MWNT/Nafion sensor properly operated at the diffusion-limited condition. This linear dependence has the advantage of easily and reliably assessing the analyte concentration. The H_2 diffusion rate into the sensing layer was controlled by the thickness and porosity of the PTFE barrier layer and nano-structural features of the Pt-MWNT sensing electrode.

Figure 5 shows a cyclic response curve of the Pt-MWNT/Nafion electrode for ten sequential 1000 ppm hydrogen exposures. Reliable detection behavior is observed with an average maximum response current of 3.57 mA. The standard deviation calculated from the repeated measurements corresponded to 1.0% variation with respect to the average maximum detection current. In addition, the average response and recovery times were found to be 33 and 28 s,

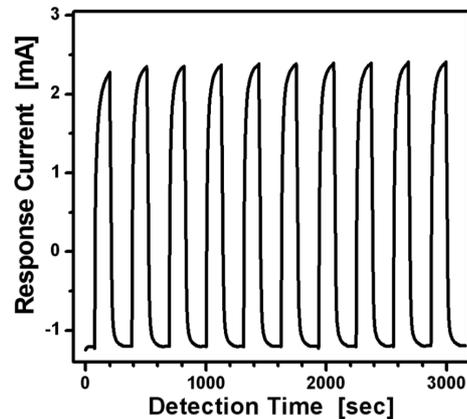


Fig. 5. An amperometric response curve of the Pt-MWNT/Nafion sensor for the repeated 1000 ppm H_2 exposures.

Table 1. Summary of material properties of the Pt-MWNT electrode

Electrode	Pt loading mg cm^{-2}	Thickness μm	Sheet resistance $\Omega \text{ sq}^{-1}$	ESA $\text{cm}^2 \text{ mg}^{-1}$
Pt-MWNT	0.12	20.0	3.0	2170

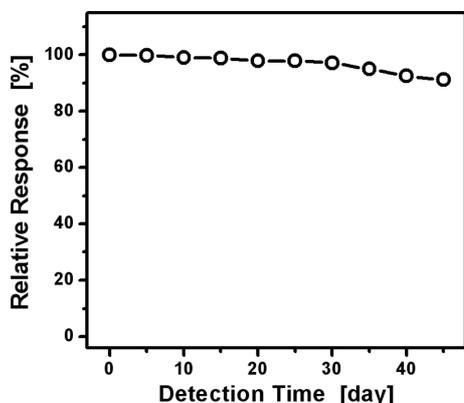


Fig. 6. Long-term variation in relative response current of the Pt-MWNT/Nafion sensor upon exposure to 500 ppm hydrogen.

respectively, where these times were defined by the T_{90} time to reach a 90% position of the maximum value. Therefore, our Pt-MWNT/Nafion sensor could give reproducible and reversible responses over a large number of detection cycles with reasonably short response and recovery times.

In order to evaluate the long-term performance of the Pt-MWNT/Nafion electrode, the response current was measured over a period of 45 days for 500 ppm H_2 exposure. Fig. 6 displays the relative response current change as a function of storage day. Little decrease in response current was observed as the time elapsed. Even after 45 days, the sensing response corresponded to 91% of the initial sensitivity. The response decrease might be interpreted as the degradation in electrocatalytic activity probably due to the surface poisoning of Pt NPs. Consequently, these results indicated that our Pt-MWNT/Nafion electrode had a fairly good long-term stability as well as detection reproducibility. Now, further researches are being focused on the development of solid-state amperometric H_2 sensors based on the Pt-MWNT/Nafion electrode.

4. Conclusions

The amperometric Pt-MWNT/Nafion electrode was successfully fabricated using the hot-pressing method. Hydrogen detection performance of this Nafion-based electrode exhibited a very high sensitivity of $3.60 \mu A ppm^{-1}$, a low LOD of about 2.0 ppm, an excellent linear response with a correlation coefficient

of 0.9997, response and recovery times of around 30 s, good reproducibility and long-term stability. These superb sensing characteristics seem to result from the following structural features of the Pt-MWNT sensing layer: the strong attachment of polycrystalline, nano-sized Pt NPs on the MWNT side wall by means of the oxygenated MWNT-assisted chemical reduction, the entangled nanoporous structure of the Pt-MWNT layer achieved through vacuum filtration, and the strong adhesion between Nafion and Pt-MWNT via hot-pressing. These results suggest that the nanostructure-controlled Pt-MWNT/Nafion electrode can provide an opportunity to fabricate a solid-state amperometric H_2 sensor of high performance with minimal use of expensive Pt sources.

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