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RESEARCH ARTICLE

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Titania-Assisted Dispersion of Carboxylated Single-Walled Carbon Nanotubes in a ZnO Sol for Transparent Conducting Hybrid Films

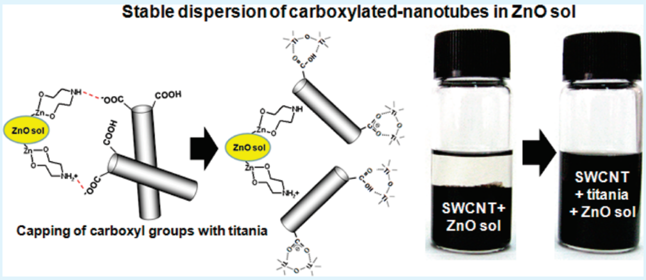
Joong Tark Han,*,[†] Bo Gyeong Kim,[†] Myung Yang,[‡] Jun Suk Kim,[†] Hee Jin Jeong,[†] Seung Yol Jeong,[†] Seong-Hyeon Hong,[‡] and Geon-Woong Lee*,[†]

[†]Nano Carbon Materials Research Group, Korea Electrotechnology Research Institute, Changwon 641-120, Korea

[‡]Department of Materials Science and Engineering and Research Institute of Advanced Materials, Seoul National University, Seoul 151-744, Korea

Supporting Information

ABSTRACT: We report a facile chemical route for stabilizing a dispersion of carboxylated single-walled carbon nanotubes (SWCNTs) in a ZnO sol. The dispersion is stabilized via capping of the carboxyl groups on the SWCNT surface by a titania layer, which was confirmed by Fourier transform infrared spectroscopy and transmission electron microscopy. We also demonstrate that the conductivity of the films prepared from the SWCNT/TiO_x/ZnO sol is dramatically enhanced by thermal treatment and that the thermal stability of the hybridized films with the ZnO sol is notably improved relative to that of a pristine SWCNT film. The structural and chemical changes of the fabricated films were characterized by Raman spectroscopy. As one application, it was presented that thermally treated SWCNT/TiO_x/ZnO hybrid thin film sensors showed hydrogen sensing characteristics even at room temperature.



KEYWORDS: single-walled carbon nanotubes, dispersion, titania, ZnO sol, thermal stability, H_2 gas sensor

1. INTRODUCTION

Single-walled carbon nanotube (SWCNT)-based transparent conductive film (TCF) technologies have potential applications in gas sensing, electrostatic dissipation, electromagnetic interference shielding, and transparent film heating, as well as in the development of alternative electrode materials for solar cells, flexible electronic devices, automobiles, optical devices, and touch panels or e-papers in display technologies.[1−8] Practical applications of SWCNT-based TCFs demand excellent thermal stability and thermohydrostatic stability to achieve long-term reliability.[9−14] The inclusion of inorganic oxides, such as SiO_2, TiO_2, ZnO, and SnO_2, enhances the stability of CNT-based films.[15−20] In addition, SWCNT films hybridized with semiconducting metal oxides or catalytic metal nanoparticles can be used as hydrogen sensors because the resistivity of the materials can change upon gas adsorption and desorption.[21−24] To fabricate SWCNT/metal oxide films by solution processes, SWCNTs should be well-dispersed in an inorganic oxide sol. In previous studies, CNTs that had been highly oxidized by acid treatment or pristine CNTs dispersed in a surfactant solution were used to form hybrid materials with metal oxides.[19,24] The surfactant used as a dispersant of the CNTs in aqueous solutions ideally should be removed. At the same time, surface functionalization of SWCNTs drastically reduces the conductivity of CNTs. The development of solution-based fabrication processes for ZnO films, in particular, should rely on the organic solvents, and CNTs should be mildly functionalized for dispersion in solvents without dispersant. Moreover, the dispersion stability of SWCNTs that are end-functionalized with carboxylate groups (SWCNT-COOH) strongly depends on the ionic strength and pH of the solution.[25−29] At pH < 3.0, SWCNTs are protonated, and they aggregate as a result of van der Waals forces and hydrogen bonding between protonated carboxylic acid groups. At pH > 3.0, mutual repulsion between tubes with charged carboxylic groups stabilizes SWCNT dispersions. Organic or inorganic materials that contain amine groups can also promote the aggregation of SWCNTs-COOH through a hydrogen-bonding network. A ZnO sol stabilized with diethanolamine for film formation can also induce severe aggregation of carboxylated SWCNTs in an organic solution due to the formation of a hydrogen-bonding network. These aggregation problems must be solved before we will be able to fabricate uniform SWCNT/ZnO hybrid films.

This work presents a facile chemical route to stabilizing carboxylated SWCNT dispersions in a ZnO sol, achieved by capping the carboxyl groups on the SWCNTs with TiO_x. The optoelectrical properties of the films fabricated from the stabilized SWCNT/TiO_x/ZnO sol solutions indicated that the films are more stable than films formed from pristine SWCNT-COOHs hybridized with SiO_2 or TiO_x sols, even after heating at 350 °C. Moreover, we found that the SWCNT/ZnO thin films

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functioned as hydrogen gas sensors, even at room temperature, because of the conducting SWCNT networks. This antiaggregation strategy has several advantages: (i) capping of the carboxylate groups on SWCNTs with TiO_x produces stable dispersions of CNTs in any desirable solution; (ii) the metal oxide layer enhances the thermal stability of the carboxylated SWCNTs at high temperatures; (iii) uniform SWCNT networks hybridized with metal oxide materials can be formed over large areas, even by spraying.

2. EXPERIMENTAL METHODS

2.1. Materials and Sample Preparation. Single-walled carbon nanotubes (P3-SWCNTs), produced by the arc-discharge method and functionalized by HNO_3 treatment, were purchased from Carbon Solution Inc. and used as received. The carboxylic groups on P3-SWCNTs were confirmed by X-ray photoelectron spectroscopy (XPS; ESCALAB 250) measurements (Figure S1 in the Supporting Information). Zinc acetate dehydrate, diethanolamine, titanium isopropoxide (TIP), acetylacetone (acac), tetraorthosilicate, and ethanol were purchased from Aldrich and used as received. A total of 20 mg of SWCNTs were dispersed in 100 mL of ethanol for 1 h in an ultrasonic bath, followed by treatment in a high-pressure homogenizer and bath sonicator. The ZnO sol was prepared using diethanolamine as a stabilizer, as described previously.[30−32] Anhydrous zinc acetate (6.6 g) and diethanolamine (3.15 g) were stirred in isopropyl alcohol for 30 min to prepare the ZnO precursor solution. For capping of the carboxyl groups on SWCNTs, TIP/acac (1:0.5 molar ratio) was added to the SWCNT dispersion solution, and the solution was stirred for 30 min, followed by the addition of a ZnO sol. To characterize the chemical structures of TiO_x-treated SWCNTs, the Fourier transform infrared (FTIR) spectra were measured by the KBr pellet method using dried SWCNT and SWCNT/TiO_x powder. The control coating solution containing TiO_x or SiO_2 sol was also prepared by the direct mixing of a SWCNT solution with the respective sol. The SiO_2 precursor sol solution was prepared by mixing 5 g of tetraethoxysilane (from Aldrich), 2 g of water, 50 mL of ethanol, and 100 μL of 12.1 M HCl, which was reacted at 60 °C for 1 h. The TiO_x sol was prepared by mixing 1 g of TIP, 1.76 g of acac, 0.25 g of water, and 20 mL of ethanol and then continuous stirring for 30 min.

2.2. Film Formation and Characterization. The fabrication of SWCNT/inorganic hybrid thin films was achieved at room temperature using an automatic spray coater (NCS Co., NCS400) with a nozzle 1.2 mm in diameter. The prepared films were then heated at selected temperatures (from 150 to 400 °C) to remove any remaining chemicals and to cure the metal oxide sol. The microstructures of the resulting films were obtained by scanning electron microscopy (SEM; Hitachi S4800). Coating of the SWCNTs with the TiO_x sol was characterized by transmission electron microscopy (TEM; JEM 2100F). The sheet resistance of the films was measured by a four-probe tester (Loresta, MCP-T610) in yellow light to exclude the photoconduction effect because the electric behavior of the ZnO and TiO_x materials can be influenced by light of shorter wavelength. The transmittance of the films was determined using a Varian Cary winRV spectrometer. The Raman spectra were measured using a high-resolution Raman spectrometer (LabRAM HR800 UV) to characterize small changes in the nanotube film state at room temperature. An excitation at a wavelength, λ, of 633 nm was used. To characterize the gas sensing properties, a pair of comblike platinum electrodes was formed by sputtering on the SWCNT/TiO_x/ZnO hybrid thin film through a mask. The gap between the platinum electrodes was 0.2 mm, and the width was 8 mm. The gold lead wires were attached to the electrodes using an silver paste. The hydrogen sensing properties were determined by measuring the changes in the electric resistance under 1000 ppm H_2 balanced with air and pure air between room temperature and 100 °C. The electrical resistance was measured using a multimeter (Keithley 2000).

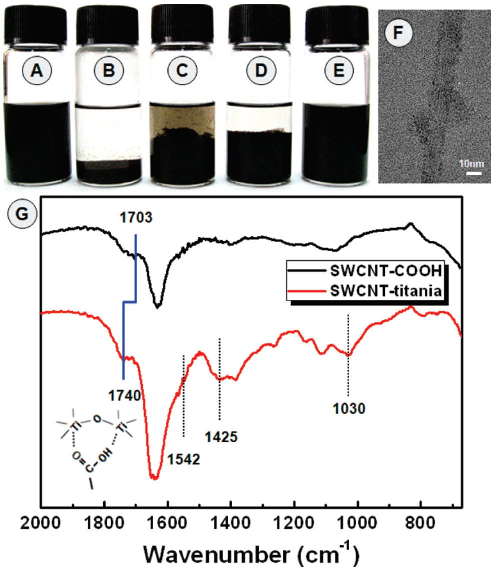


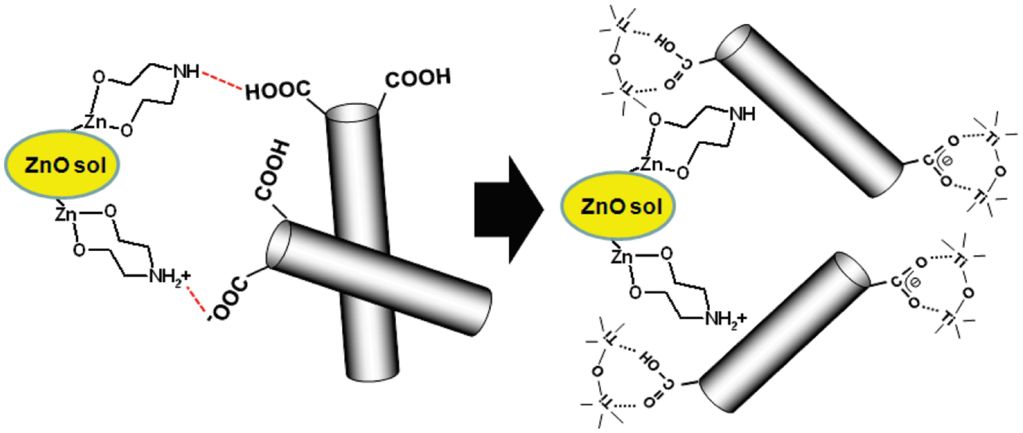
Figure 1. Photographs of vials containing SWCNTs dispersed in ethanol (a) before and after the addition of (b) zinc acetate dihydrate, (c) diethanolamine, and (d) ZnO sol. (e) The rightmost vial contains SWCNTs stabilized by a TiO_x sol in a ZnO sol. (f) TEM image of a SWCNT bundle coated with TiO_x. (g) FTIR spectra of pristine SWCNTs and TiO_x-treated SWCNTs.

3. RESULTS AND DISCUSSION

The stabilities of the dispersions were investigated by observing precipitates visually and by monitoring the UV−vis spectrum. As shown in Figure 1, the addition of zinc acetate dihydrate (a precursor for a ZnO sol) to a SWCNT solution induced severe aggregation, resulting in the precipitation of SWCNTs. Diethanolamine also disrupted the solution stability. Interestingly, the addition of a ZnO sol to the SWCNT solution yielded nanotube precipitates, but these precipitates were present in a swollen state, and the aggregates were interconnected by a ZnO sol network. Such precipitates were also observed upon the addition of a binder material containing amine groups, such as aminopropylsilane. Therefore, we suggested that SWCNT-COOH aggregation was facilitated by the formation of a hydrogen-bonding network with the amine groups of the ZnO sol, as shown in Scheme 1. The volume of the nanotube precipitates produced by the addition of the ZnO sol was larger than the volume of the precipitates produced by the addition of zinc acetate dihydrate, implying that separate zinc ions (Zn^{2+}) and acetate ions (CH_3COO^-) could not bridge the nanotubes.

To resolve the problem of aggregation via the formation of an extended hydrogen-bonding network, we proposed a method for passivating the carboxylic groups on the SWCNTs using a TiO_x sol prepared from a TIP/acac solution, as shown in Scheme 1. We used the fact that two carboxyl groups can bridge two titanium atoms.[33,34] To optimize the quantity of TIP required for passivation of the carboxylic groups in the SWCNTs, various quantities of the TIP/acac solution were added to a SWCNT-COOH solution, and the solution was stirred for 30 min. We found that 50 wt % TIP was the minimum concentration required for stabilizing of the SWCNT solution after the addition of the ZnO sol. The quantity of TIP required depended on the number of carboxylic groups available to interact with the TiO_x sol. The TiO_x sol stabilizer, acac, was also optimized because TIP

Scheme 1. **Proposed Mechanism for the Improved Stability of Dispersion of Carboxylated SWCNTs in a ZnO Sol Achieved by Capping of the Carboxyl Groups with a TiO_x Sol**



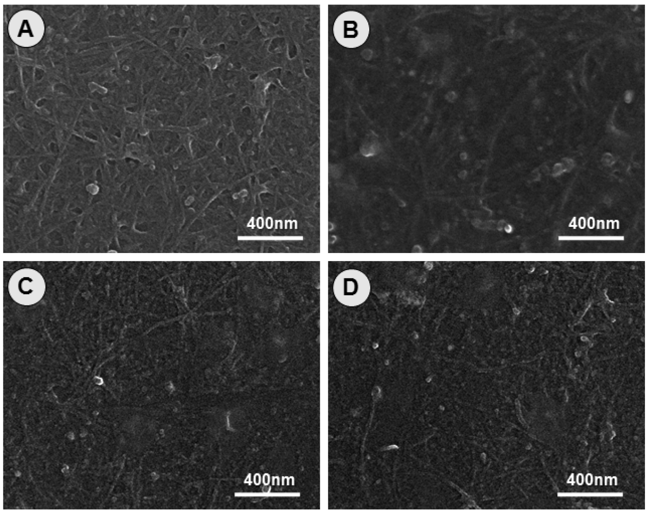


Figure 2. SEM images of SWCNT/TiO_x/ZnO hybrid films after heating at (a) 150, (b) 300, (c) 350, and (d) 400 °C.

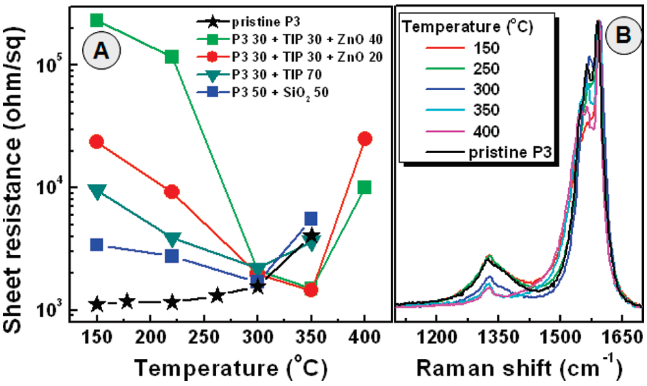


Figure 3. (a) Sheet resistance as a function of temperature for films composed of pristine SWCNTs and SWCNTs hybridized with the TiO_x sol, SiO_2 sol, or the TiO_x/ZnO sol showing 87% transmittance at 550 nm wavelength. The values in the legend indicate the weight percent of each material. (b) Raman spectra of a pristine SWCNT film and SWCNT/TiO_x/ZnO hybrid films after thermal treatment at selected temperatures.

easily forms gel and precipitates in the absence of acac. In this study, a 1:0.5 molar ratio solution of TIP/acac was used to selectively passivate the carboxylate groups on the nanotube surfaces. The FTIR spectrum in Figure 1g clearly shows that the SWCNT-COOHs bridged two titanium atoms with one carboxylate group. The vibrational peak of the carboxylic groups on the SWCNTs shifted from 1703 to 1740 cm^{-1}, which suggested that the TiO_x sol acted as a selective capping material for the carboxylated SWCNTs. TEM images, as shown in Figure 1f, also indicated that TiO_x formed on the SWCNT surface. As shown in Figure 1e, a stable dispersion of SWCNTs was successfully achieved in a solution containing the ZnO sol and TIP/acac. The linear relationship between absorbance and concentration for the SWCNT/TiO_x/ZnO solution agreed well with the Beer–Lambert law, indicating that the prepared solution was stable (Figure S2 in the Supporting Information).

We used a simple spray coating in order to fabricate the pristine SWCNT (Figure S3 in the Supporting Information) and SWCNT/TiO_x/ZnO thin films with a transmittance at 550 nm of 78–97%, and the films were thermally treated to remove diethanolamine and to crystallize the ZnO sol. Thereafter, the films showing 87% transmittance at 550 nm wavelength were used in order not to change the amount of SWCNTs in the films. Energy-dispersive X-ray spectroscopy (EDAX) was used to confirm the presence of titanium, oxygen, zinc, and carbon in the SWCNT/TiO_x/ZnO film (Figure S4 in the Supporting Information). Figure 2 shows SEM images of the film after thermal treatment at selected temperatures. After heating at 300 °C, the film surface became smoother than the surface of the film heated at 150 °C because the evaporation of diethanolamine at 300 °C promoted the organization of the TiO_x/ZnO sol at the surface layer. Heating beyond 300 °C induced crystallization of the ZnO sol.[30−32] SEM images indicated the formation of ZnO aggregates on the SWCNT surfaces after heating at 350 and 400 °C. The thermal stability of the prepared films was investigated by measuring the sheet resistance of the films after heating at selected temperatures, as shown in Figure 3a. SWCNT/TiO_x and SWCNT/SiO_2 hybrid films were also prepared as controls. After heating at 150 °C, the sheet resistance of the SWCNT/SiO_2 film was smaller than the sheet resistances of SWCNT/TiO_x and SWCNT/TiO_x/ZnO hybrid films because of the absence of a stabilizer (i.e., acac in the TiO_x sol or diethanolamine in the ZnO sol). Heating at 300 °C increased the sheet resistance of pristine SWCNT films due to a thermal oxidation as determined by thermogravimetric analysis (TGA) and Raman spectroscopy (Figure S5 in the Supporting Information). However, heating dramatically decreased the sheet resistance of films formed from the SWCNTs hybridized with inorganic oxide sols because of the protection of the nanotubes and removal of stabilizers at temperatures above 200 °C, confirmed by TGA (Figure S6 in the Supporting Information) and shown in Figure 3a. Notably, the TiO_x/ZnO sol dramatically enhanced the thermal stability of the material at temperatures exceeding 300 °C. As reported previously,[35] SiO_2 sol binders can minimize the increase in the junction resistance by introducing an unfavorable interaction between CNTs and the SiO_2 sol in a hybrid film. However, bare SWCNTs are exposed to air (Figure S7a in the Supporting Information), which reduced the thermal stability of these materials at high temperatures. Furthermore, the porous network structure of the SWCNT/TiO_x films (Figure S7b in the Supporting Information) was detrimental to the thermal stability of the films at temperatures above 300 °C.

Raman spectra were measured at 633 nm excitation to observe small variations in the SWCNT/TiO_x/ZnO hybrid films produced as a result of thermal treatment. Figure 3b shows the typical D and G bands of a Raman spectrum of pristine SWCNT and SWCNT/TiO_x/ZnO hybrid films after thermal treatment at selected temperatures. The D band in the Raman spectra of functionalized SWCNT samples contained a broad peak upon which was superimposed a sharp peak. The broad feature arose from the amorphous carbon, and the sharper feature arose from the CNTs.[36] The D band of the hybrid film was narrowed, and the I_D/I_G ratio decreased dramatically from 0.18 to 0.07 after heating at 400 °C. These spectral changes corresponded to the removal of the broad amorphous carbon peak that underlay the relatively sharp SWCNT feature. The sheet resistance of SWCNT/TiO_x/ZnO hybrid films also decreased. The 1.96 eV laser excited the metallic SWCNTs, as demonstrated by the presence of a large Breit−Wigner−Fano (BWF) line at the lower energy side of the G band in Figure 4. The BWF component changed upon thermal treatment at higher temperatures. Heating at 150 °C resulted in the development of more BWF components at lower energies because of the presence of electron-donating diethanolamine species.

On the other hand, heating at 300 °C produced BWF components that were similar to those of pristine SWCNTs. Additional BWF components were developed after heating to temperatures above 300 °C because the crystallized ZnO acted as an n-type semiconductor.[30−32] Therefore, the sheet resistance was expected to increase upon thermal treatment at temperatures above 300 °C. However, the sheet resistance of the film decreased upon heating at 350 °C, despite the n doping with ZnO. The thermal purification of SWCNTs may have compensated for the n-doping effects. Moreover, the sheet resistance of a film containing a ZnO sol increased further upon heating at 400 °C because of the electron-donating character of further crystallized ZnO, even though the SWCNTs were not oxidized. Under ambient conditions, nanotubes usually show p-type behavior because of the presence of oxidizing adsorbates. The exposure of nanotubes to materials with electron-donating groups provides extra electrons to the semiconducting SWCNTs. This compensates for the p-doping effects and produces a dedoping effect[37−39] that either recovers an intrinsic Fermi level or converts the behavior to n doping after hybridization. The Fermi level discussed here were shifted to a higher value. The number of hole carriers was reduced upon dedoping, and the intrinsic resistance of the SWCNTs increased.

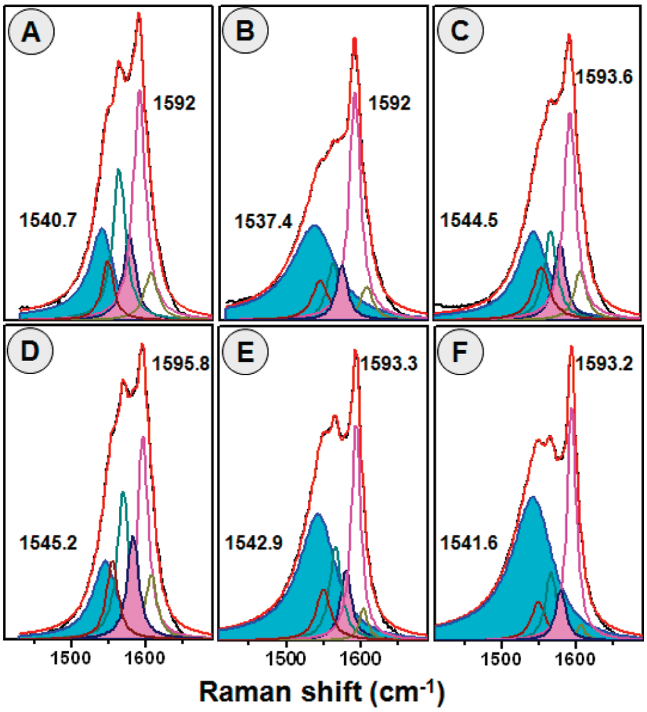


Figure 4. Deconvolution of the G band into one metallic component (shaded area in pink), one metallic BWF component (shaded area in blue), and four semiconducting components (open area) at an excitation energy of 1.96 eV: (a) pristine SWCNT film; SWCNT/TiO_x/ZnO hybrid films heated at (b) 150, (c) 250, (d) 300, (e) 350, and (f) 400 °C. The values indicate the peak positions of the BWF line and the G^+ line.

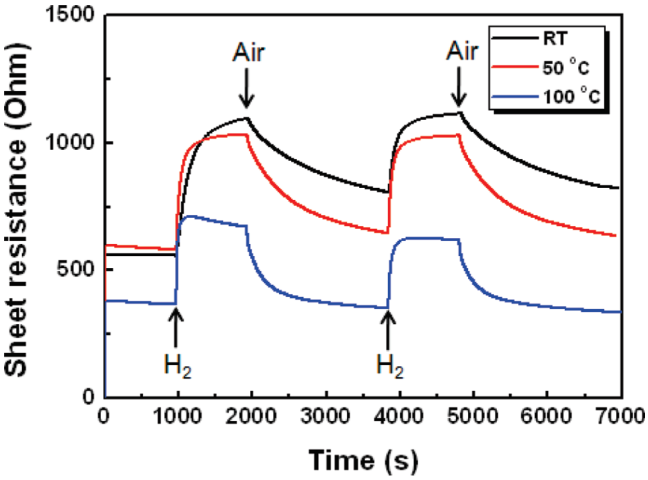


Figure 5. Response transient of a SWCNT/TiO_x/ZnO (30/30/40 wt %) thin film sensor toward 1000 ppm H_2 as a function of the sensing temperature.

Figure 5 shows the response transients of SWCNT/TiO_x/ZnO thin film sensors upon exposure to 1000 ppm H_2 balanced with air as a function of the sensing temperature. The SWCNT/TiO_x/ZnO thin film sensors reversibly responded to H_2 gas even at room temperature. The resistance increased rapidly upon exposure to H_2 gas and recovered rather slowly upon exposure to air. As the temperature was increased, the gas response became more stable and the response time decreased. SWCNTs, themselves, are not sensitive to H_2 gas,[23] and it is thought that ZnO recognizes H_2 gas, thereby acting as a receptor in the SWCNT/TiO_x/ZnO sensor. The resistance of the sensor was 100−1000 Ω in air, which is several orders of magnitude lower than that of ZnO thin films or nanostructures.[40] This indicates that the current path is along the SWCNT network rather than through ZnO. This cooperative combination permits hydrogen detection even at room temperature, with a relatively fast response.[41] Recently, a conductive ZnO nanorod-coated fabric was fabricated, and room temperature H_2 gas sensing was demonstrated. However, the resistance of the fabric sensors was too high ($\sim 10^{10}$ Ω), and the response was rather slow.[42,43] The film sensor exhibited p-type semiconductor sensing behavior. SWCNTs tend to behave as p-type semiconductors, with hole transport as the dominant process,[44] and ZnO behaves as an n-type semiconductor. The surfaces of ZnO are generally covered with negatively charged adsorbed O^- ions. The negatively charged surface layer results in an electron depletion layer just below the surface, which acts as a potential barrier for electronic conduction.[45] Upon exposure to H_2, the O^- adsorbates may have reacted with H_2 gas and released electrons to the conduction band of SnO_2, which then transferred electrons to SWCNTs and lowered the hole carrier concentration. As a result, the resistance of the SWCNT/TiO_x/ZnO sensor increased, as observed in Figure 5. The gas sensing behavior of SnO_2/SWCNT network sensors has been shown to change from p-type to n-type upon introduction of a surface coverage of the SnO_2 surface layer on the SWCNTs.[46] Thus, it is proposed that SWCNTs were not fully covered with ZnO exhibiting p-type sensing behavior.

In this study, we have proposed a method for fabricating SWCNT/ZnO hybrid films with a dispersion-stabilized SWCNT/ZnO sol mixture solution, which can be operated even at room temperature. Our strategy for stabilizing the functionalized CNTs in solution provides clues to solving the dispersion problem for CNT/metal oxide sol mixture solutions for the fabrication of CNT-based hybrid thin films in electronic applications.

4. CONCLUSIONS

We have presented a facile strategy for preparing a stabilized dispersion of carboxylated SWCNTs in a ZnO sol via capping of the carboxyl groups with the TiO_x sol. The efficient passivation of carboxyl groups with the TiO_x sol was confirmed by FTIR spectroscopy and TEM. We also demonstrated that the thermal stability of the films improved notably following hybridization with the ZnO sol relative to the stability of SWCNT/SiO_2 and SWCNT/TiO_x hybrid films. This high thermal stability could be attributed to crystallization of the ZnO sol, even at 400 °C without thermal oxidation of nanotubes. Moreover, SWCNT/TiO_x/ZnO thin film sensors were found to respond to H_2 gas, even at room temperature, which indicated that ZnO was sensitive to the H_2 gas and SWCNTs provided a conducting path (transducer function). The H_2 gas response of the films was typical of p-type behavior.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. XPS spectrum of pristine SWCNTs, UV absorbance of a SWCNT/TiO_x/ZnO solution, transmittance versus sheet resistance plot of a SWCNT-COOH film, EDAX spectrum of a SWCNT/TiO_x/ZnO film, and TGA graph and Raman spectra for pristine SWCNT and SWCNT/TiO_x/ZnO films. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jthan@keri.re.kr (J.T.H.), gwleephd@keri.re.kr (G.-W.L.). Tel: +82-55-280-1677. Fax: +82-55-280-1590.

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