Differentiation of Gas Molecules Using Flexible and All-Carbon Nanotube Devices

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · DECEMBER 2007

Impact Factor: 4.77 · DOI: 10.1021/jp710362r

THE JOURNAL OF PHYSICAL CHEMISTRY C LETTERS

2008, *112,* 650−653
Published on Web 01/01/2008

Differentiation of Gas Molecules Using Flexible and All-Carbon Nanotube Devices

Dongliang Fu,[†] Hueiling Lim,[†] Yumeng Shi,[†] Xiaochen Dong,[†] S. G. Mhaisalkar,[†] Yuan Chen,[‡] Shabbir Moochhala,[§] and Lain-Jong Li*,[†]

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Ave., Singapore 637819, School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, and DSO National Laboratories, 20 Science Park Drive, Singapore 118230, Singapore

Received: October 26, 2007; In Final Form: December 2, 2007

Carbon nanotubes (CNTs) are extremely sensitive to the electronic perturbations from environmental gases. However, the electrical detection of carbon monoxide (CO) is still a challenge. Here we show that 1 ppm of CO can be electrically detected at room temperature using a CNT resistor and the detection is proposed related to the sidewall functionalities (COOH). A simple all-CNT electronic nose composed of two resistors (or one resistor plus one transistor) is able to differentiate CO and other oxidative gases (for example NO and NO_2). The electronic nose is working on both conventional SiO_2/Si and flexible substrates.

The detection of gases and chemical vapors using single-walled carbon nanotubes (SWNTs) has been a subject of active research recently. Kong et al. first demonstrated the sensing of NO_2 and NH_3 based on transport measurements,[1] which opened the routes of electrical sensing using carbon nanotubes (CNTs). Snow et al. later reported the use of SWNT random networks for selective detection of chemicals.[2] The observed responses in previous research were attributed to the adsorption of analytes on CNT sidewall,[1−3] charge transfer (electronic doping),[4] modification of the CNT−electrode interface[5−6] or interaction of the analyte with sidewall defects.[7] Although significant numbers of biomolecules, gases, or chemical vapors have been successfully detected by SWNT conductance change,[8] the electrical detection of carbon monoxide (CO) is still a challenge.[9−10] Carbon monoxide is known as an odorless and poisonous gas present in the environment. The health effects of CO depend on the level of CO and time of exposure. Normally as CO levels increase above 150−200 ppm, disorientation, unconsciousness, and death are possible. The sensing of CO is therefore critically important for environmental monitoring. Recently solid-state sensors toward selective CO detection have been reported using inorganic metal oxides,[11−14] where the combustible gas CO reacts with pre-adsorbed oxygen species on surfaces of metal oxides and results in the change of their conductance. These sensors require a high operation temperature normally beyond 200 °C, which is one of the major obstacles toward low-power consumption or flexible sensor devices. The reported CO detection limit for these devices is typically larger than 100 ppm. A very recent study using a single SnO_2 nanowire as the electrical transducer has improved the CO detection limit down to 5 ppm[14] although the high-temperature detection is still required. In this letter, we report several advances in gas sensing; (1) Very low concentration (∼ 1 ppm) of CO can be electrically detected at room temperature using all-SWNT (contact pads and channel are all made of SWNTs) resistors, where the detection is proposed related to the sidewall defects (COOH group). (2) SWNT resistors and transistors can easily detect oxidative gases (NO and NO_2) regardless of their surface functionalities but the resistors or transistors made from SWNT without COOH functionalities were insensitive to CO exposure. Therefore, a simple all-SWNT sensing device composed of two resistors (with and without COOH functionalities) or one resistor (with COOH functionalities) plus one transistor (without COOH functionalities) is able to differentiate CO and oxidative gases. (3) We also demonstrate that the electrical differentiation is workable on both conventional SiO_2/Si and flexible substrates. The success of the selective detection of gases on flexible substrates further demonstrates the possibility of using SWNTs in the applications for low-power consumption, bendable and lightweight sensor techniques.

The SWNTs used for experiments (P2-SWNT and P3-SWNT) were arc-discharge produced and purchased from Carbon Solutions, Inc. (U.S.A.). According to the provider, P3-SWNT is nitric acid treated and remains highly COOH functionalized (∼4 to 6 atomic % of COOH). By contrast, the P2 material closely approximates the pristine state with low functionality and low chemical doping. To ensure the removal of COOH and other defects, P2-SWNTs were further annealed at 900 °C in Ar atmosphere for 1 h prior to use. We have also used another two types of SWNTs with low functionalities: HiPCO (from Carbon Nanotech. Inc.) and homemade pristine arc tubes (arc-SWNTs), where the arc-SWNTs were synthesized using a standard catalytic arc process. The obtained P2-SWNTs (or HiPCO or arc-SWNTs) were dispersed in aqueous sodium dodecylbenzene sulfate (SDBS) suspensions with 30 min probe sonication (Sonics & Materials Inc., model VCX 130), followed by ultracentrifugation at 53000*g*. P3-SWNTs were directly

* To whom correspondence should be addressed. E-mail: ljli@ntu.edu.sg.
[†] School of Materials Science and Engineering, Nanyang Technological University.
[‡] School of Chemical and Biomedical Engineering, Nanyang Technological University.
[§] DSO National Laboratories.

10.1021/jp710362r CCC: $40.75

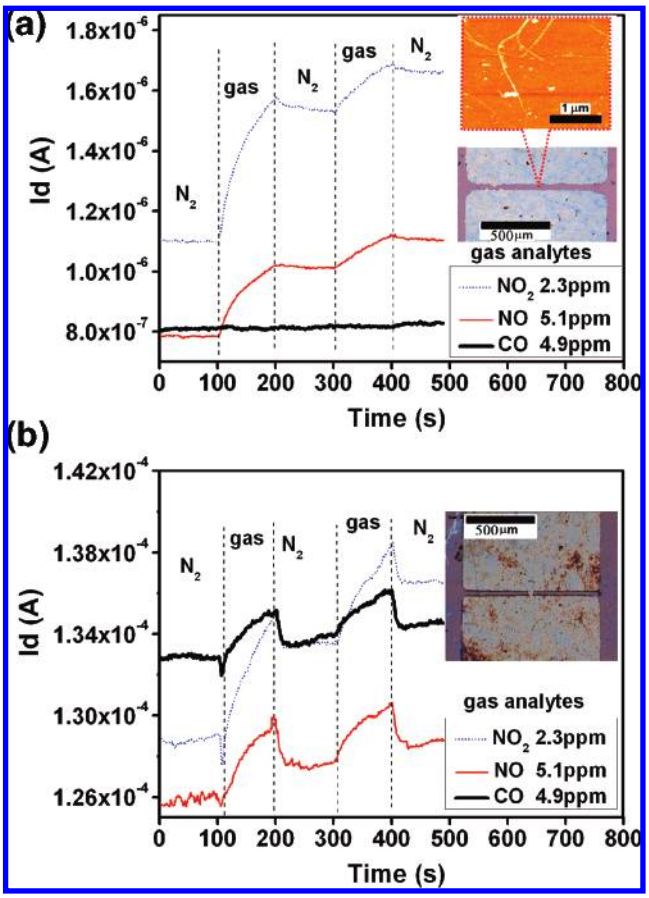

Figure 1. (a) Sensing curves (I_d vs gas switching cycles) for an all-SWNT transistor (P2-SWNTs as channel materials) upon exposure to CO, NO and NO_2 respectively ($V_g = -10$ V and $V_d = 10$ V). The top of the inset shows the AFM image of the carbon nanotubes in the channel area and the bottom of the inset shows the optical image of the device. (b) Sensing curves for an all-P3-SWNT resistor upon exposure to CO, NO, and NO_2 respectively ($V_d = 10$V). The inset shows the optical image of the resistor. All devices are formed on a Si-backgate structure.

dispersed in pure water following the same sonication and centrifugation procedures. The SWNT solutions were then sprayed on to the photoresist patterned substrates to form either a resistor structure or merely CNT electrodes for further transistor fabrication. The typical procedure for transistor fabrication is as follows: arc-SWNTs (or HiPCO or P2-SWNTs) suspensions were drop-cast on to the CNT electrodes, followed by deionized water rinsing, and air blow-drying. We note that it is not relatively easy to obtain transistor characteristics using P3-SWNTs as channel materials because the P3-SWNTs tend to aggregate into bundles via hydrogen bonding. All electrical measurements were performed on a standard electrical probe station enclosed in a 200 L glove box under nitrogen atmosphere. Pure nitrogen (>99.9995%), CO (4.9 ppm in pure N_2; National Oxygen Pte Ltd.; certified with gas chromatography), NO, NO_2, or premixed gases to the desired concentration were then introduced through a gas nozzle (1 mm diameter) located 3 mm above the devices. The total gas flow for all experiments is fixed at 500 sccm.

We first discuss the transistor component of the all-SWNT sensing devices, where we identify this component as NO- (and NO_2-) sensitive but CO-insensitive. Figure 1a shows the sensing curves (drain current (I_d) evolution vs gas switching cycles) for an all-SWNT transistor upon exposure to CO, NO, and NO_2, respectively, where the measurements were performed at gate voltage (V_g) = −10 V and drain voltage (V_d) = 10 V. The inset in Figure 1a shows the AFM and optical images of the device where the P2-SWNTs were drop-cast on to the channel between two air-sprayed P3-SWNT pads on SiO_2/Si. Three types of SWNTs with relatively low COOH content (compared with P3-SWNT), including P2-SWNTs, HiPCO, and arc-SWNTs have been used to form the conduction channel of the transistors via drop-cast methods. The typical electrical characteristics including transfer curves and $I_d - V_d$ relations for the all-SWNT transistor (P2-SWNT as the channel materials) are shown in Figure S1a in the Supporting Information, where we observe that it behaves as a *p*-typed transistor in an ambient or N_2 environment. Figure 1a demonstrates that no detectable I_d change is observed upon CO exposure for the all-SWNT transistors. By contrast, they show pronounced I_d increases upon exposure to NO or NO_2, a behavior which is similar to the metal-contacted SWNT transistors. It is noted that the I_d increase for metal-contacted CNT transistors has been attributed to both the channel doping effect and the change in the metal−SWNT interface.[5−6] We show in Figure S1b, in the Supporting Information, that the threshold voltage (V_{th}) of the all-SWNT transistor is positively shifted upon exposure to NO, corroborating that SWNTs are doped with holes. Thus, the hole-doping of SWNTs may be the dominant mechanism for NO and NO_2 sensing although we still cannot exclude the possibility that the junction between CNT pads and the tip of the electrical probing system could also contribute to the sensing.

Now we discuss the resistor component of the electronic nose. Figure 1b shows the sensing curves (I_d vs gas switching cycles) for an all-P3-SWNT resistor upon exposure to CO, NO, and NO_2, respectively. The inset shows the image of the resistor which was formed by direct air-spraying of P3-SWNT solutions on to a photoresist patterned SiO_2/Si substrate, followed by lift-off process. The typical electrical characteristics, I_d vs V_g and I_d vs V_d for the resistor were shown in Figure S2. There is no transistor-type of gate dependence observed for I_d and the resistance of the devices is normally in the range of 0.02−0.51 MΩ. The striking effect we observe from the all-P3-SWNT resistor is that they can electrically detect the CO in addition to NO and NO_2 gases and the lowest CO concentration detectable is around 1 ppm, as shown in Figure 2. The change in I_d is suspected from the interaction between CO and the carboxylic acid group (COOH or defect site) on SWNT sidewalls. It has been reported that the CO gas can be absorbed on carboxylic acid functionalities through weak hydrogen bonding,[15] as schematically plotted in Figure 2b. We notice that the formation of hydrogen bonding between water and CO has been reported.[16] The observation of CO detection is supported by theoretical studies on various types of covalently functionalized SWNTs, according to which the main effect of the attached functionalities is to introduce sp3-bonded carbon centers which induce impurity states near the Fermi level that act as scattering centers.[17] The interaction between CO and carboxylic groups on SWNT sidewall may alter the carrier scattering probability and change the resistance of the SWNT devices. Very recently the gas adsorption at the defect sites of SWNT has been reported to produce a large electronic response experimentally[7,18] and theoretically,[7,19−20] and the functionalized metallic SWNT device has also been used as a pH sensor where the defect sites on tube sidewall increases the sensitivity.[21] To verify whether the COOH functionality plays the role in CO detection, we fabricate all-P2-SWNT resistors on SiO_2/Si, where the whole resistor is composed of P2-SWNT and no COOH functionalities exist. The device shows similarly strong response to NO and NO_2 but no

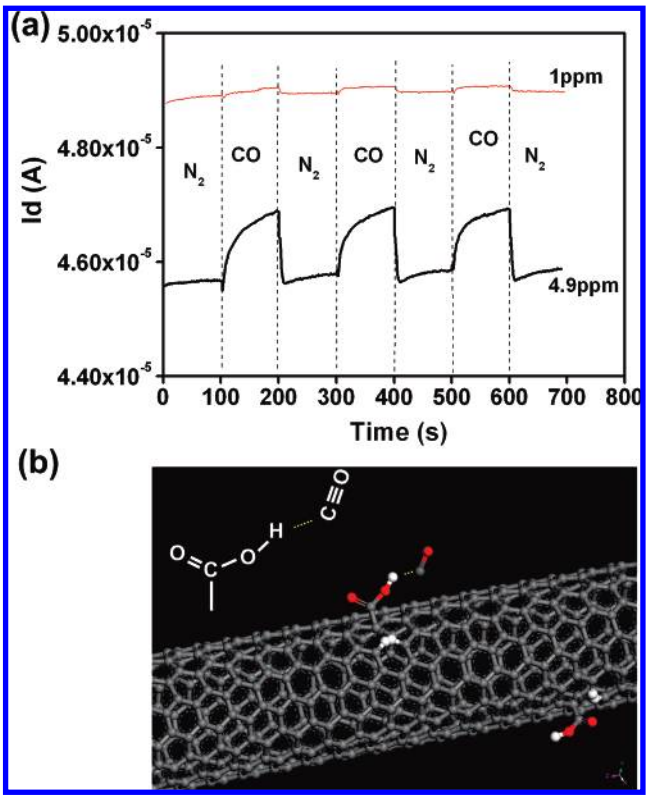

Figure 2. (a) Sensing curves (I_d vs gas switching cycles) for an all-P3-SWNT Resistor upon exposure to 5 and 1 ppm of CO ($V_g = -10$ V and $V_d = 10$ V). (b) Illustration of molecular model for CO binding to the carboxylic functionality on the sidewall of a SWNT.

response to CO at all. This corroborates that the CO detection is due to the COOH functionality. We have also fabricated the resistors formed by other type of tubes, where we first air-sprayed the P3-SWNT pads on substrates then drop-cast P2-SWNTs (or arc-SWNTs or HiPCO) on the channel area, followed by water rinsing. These devices are normally much less sensitive to the CO exposure, where we believe the resistance is dominantly contributed from the tubes in the channel area, where the tubes are with low content of COOH functionalities), and therefore, the sensitivity to CO is greatly decreased, which further strengthens the argument that the COOH functionality is crucial to the CO sensing. To understand the role of SWNT pads, we have also fabricated the Au-contacted resistor devices with similar resistance, where we first evaporated Au electrodes on substrates then air-sprayed (or drop-cast) the P3-SWNTs in the channel area. This device is normally insensitive to CO exposure, and the typical sensing curve is shown in Figure S3, in the Supporting Information. This result could suggest that the Au−SWNT contact dominates the resistance[22] of the resistor devices and the Au−SWNT contact resistance is not sensitive to CO adsorption. Therefore, SWNT pads are key elements for CO detection, and the all-P3-SWNT resistor device is identified as a good candidate for CO sensing. Based on the results we have discussed, the simple all-SWNT sensing device composed of two resistors (P3-SWNT and P2-SWNT as channel materials respectively) or a transistor together with an all-P3-SWNT resistor is proposed for differentiating CO and oxidative gases (NO or NO_2).

The selective detection of CO is not only working on conventional SiO_2/Si structures. We have demonstrated the success of using an all-SWNT gas sensor on flexible polyethylene terephthalate (PET) substrates. Figure 3 schematically illustrates the fabrication processes of the resistor-type of electronic sensors on flexible substrates. The PET substrates were coated with the positive-type of photoresist (EPG-510) and exposed to UV light for pattering. Part of the substrate was covered by a free-standing polydimethyl siloxane (PDMS) film, and the P2-SWNT solution was then air-sprayed on the open area of the photoresist patterned PET substrates, followed by immersing it in water and air drying. The PDMS film was then moved to cover the area where P2-SWNT was sprayed, and the P3-SWNT solution was then sprayed on to the rest of the pattern, followed by photoresist lift-off. The sensing results for the flexible electronic sensor are shown in Figure 4. In general the sensing behaviors of the flexible sensor devices are quite reproducible. For the 6

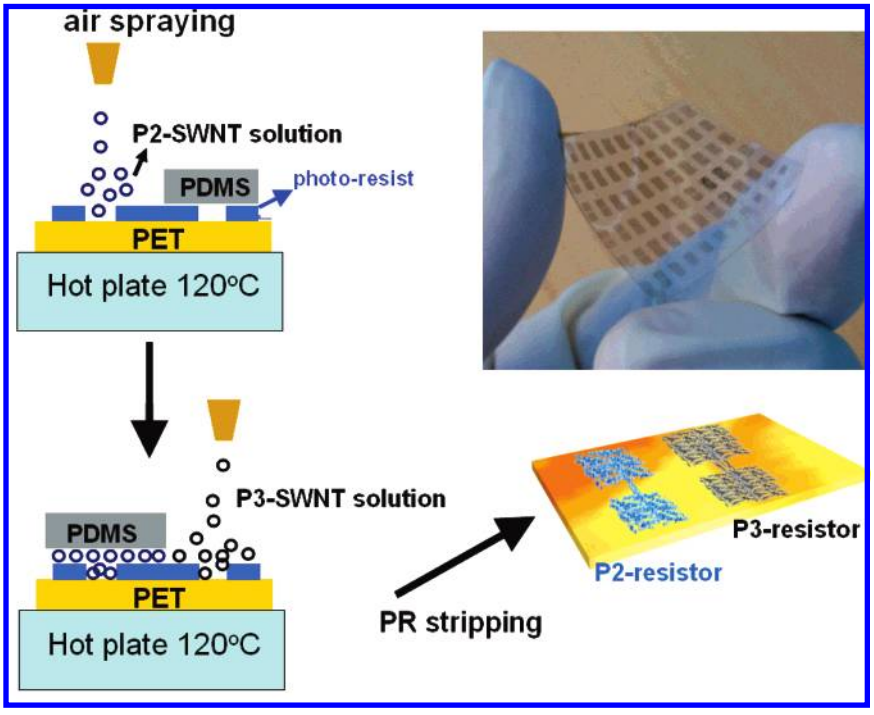

Figure 3. Schematic illustration of the fabrication processes for resistor type of sensors on PET substrates.

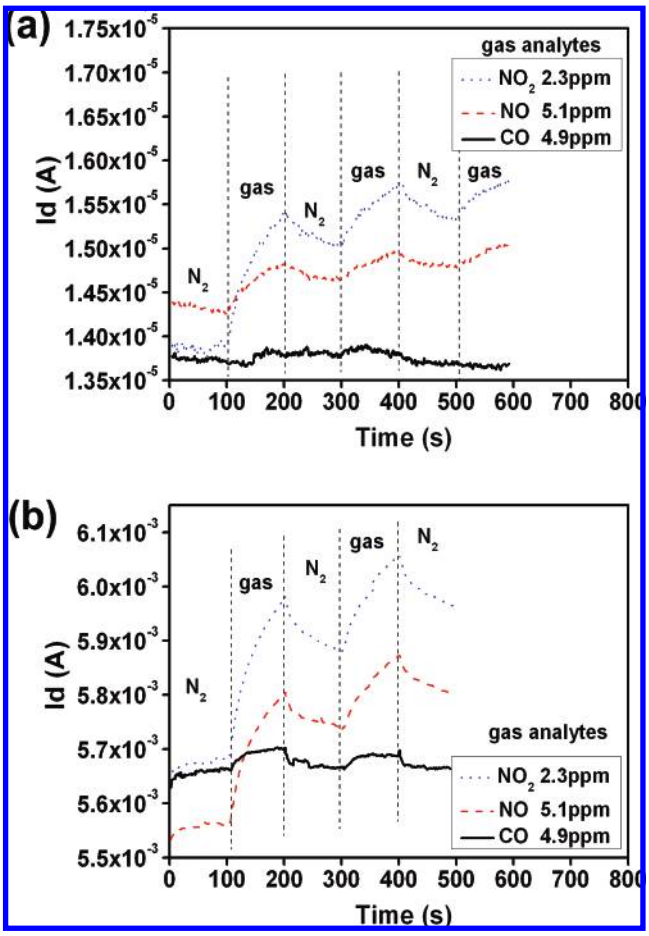

Figure 4. (a) Sensing curves for a flexible, all-P2-SWNT resistor upon exposure to CO, NO, and NO_2 respectively (V_d = 10V). (b) Sensing curves for a flexible, all-P3-SWNT resistor upon exposure to CO, NO, and NO_2 respectively (V_d = 10 V). Combination of these two devices demonstrates the possibility to differentiate CO and NO gases.

electronic sensors we have tested, they have shown consistent differentiation of CO and NO (or NO_2), similar to that on the SiO_2/Si structure. This also confirms that the interface between dielectrics (e.g., SiO_2) and SWNTs is not responsible for the gas sensing and the sensing is directly originated from the SWNTs as proposed.

In summary, we have demonstrated that the electrical detection of a low concentration of CO can be achieved at room temperature using a simple all-SWNT resistor made from COOH-functionalized SWNTs. The detection limit is around 1 ppm for CO, and the device can be re-used. A simple electronic nose composed of two resistors (respectively from P2-SWNT and P3-SWNT) is proposed to differentiate CO and oxidative gases. The electronic sensor can be fabricated on SiO_2/Si or flexible PET substrates. The electrical detection of these electronic sensors is reproducible in a well controlled gas environment, i.e, in the case when the gas analyte is only composed of pure N_2 and targeting gas. The results demonstrate the concept of using defected SWNTs as the single components for electronic noses. Our preliminary results on other defected tubes (heteroatom doped SWNTs) suggest that other toxic gases such as H_2S may be recognized. It is noticed that the moisture level also plays an important role in gas sensing, which may affect the result of quantitative detection for CO. Technically, the effect of moisture can be removed by heating the devices or using a moisture filter. The effect of moisture, temperature and also the possibility of detecting gas mixtures are under explorations in our group. In addition, we believe the approach of using different defected SWNTs is likely opening the possibility of fabricating more delicate electronic noses capable of differentiating more gas species.

Acknowledgment. This research was supported by Nanyang Technological University, Singapore.

Supporting Information Available: Transfer curves, typical electrical characteristics, and sensing curves for SWNT sensors. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *87*, 622− 625.
(2) Snow, E.; Perkins, F.; Houser, E.; Badescu, S.; Reinecke, T. S*cience* **2005**, *307*, 1942.
(3) Snow, E.; Perkins, F. *Nano Lett.* **2005**, *5*, 2414−2417.
(4) Chakrapani, N.; Zhang, Y. M.; Nayak, S. K.; Moore, J. A.; Carroll, D. L.; Choi, Y. Y.; Ajayan, P. M.; Gao, N. C. *J. Phys. Chem. B* **2003**, *107*, 9308- 9311.
(5) Zhang, J.; Boyd, A.; Tselev, A.; Paranjape, M.; Barbara, P. *Appl. Phys. Lett.* **2006**, *88*, 123112.
(6) Fu, D. L.; Xu, Y. P.; Li, L. J.; Chen, Y.; Mhaisalkar, S. G.; Boey, F. Y. C.; Lin, T. W.; Moochhala, S. *Carbon* **2007**, *45*, 1911−1920.
(7) Robinson, J A.; Snow, E. S.; Badescu, S. C.; Reinecke, T. L.; Perkins, F. K. *Nano Lett.* **2006**, *6*, 1747−1751.
(8) Sinha, N.; Ma, J.; Yeow, T. W. *J. Nanosci. Nanotechnol.* **2006**, *6*, 573−590.
(9) Santucci, S.; Picozzi, S.; Gregorio, D. D.; Lozzi, L.; Cantalini, C.; Valentini, L.; Kenny, J. M.; Delley, B. *J. Chem. Phys.* **2003**, *119*, 10904−11910.
(10) Star, A.; Joshi, V.; Skarupo, S.; Thomas, D.; Gabriel, J. C. P. *J. Phys. Chem. B* **2006**, *110*, 21014−21020.
(11) Law, M.; Kind, H.; Messe, B.; Kim, F.; Yang, P. *Angew. Chem.* **2002**, *114*, 2511.
(12) Kolmakov, A.; Klenov, D. O.; Lilach, Y.; Stemmer, S.; Moskovits, M. *Nano Lett.* **2005**, *5*, 667.
(13) Yamaura, H.; Tamaki, J.; Moriya, K.; Miura, N.; Yamazoe, N. *J. Electrochem. Soc.* **1996**, *143*, L36.
(14) Hernandez-Ramirez, F.; Tarancon, A.; Casals, O.; Arbiol, J.; Romano-Rodriguez, A.; Morante, J. R. *Sens. Actuators B* **2007**, *121*, 3.
(15) Matranga, C.; Bockrath, B. *J. Phys. Chem. B* **2005**, *109*, 4853-4864.
(16) Yaron, D.; Peterson, K. I.; Zolandz, D.; Klemperer, W.; Lovas, F. J.; Suenram, R. D. *J. Chem. Phys.* **1990**, *92*, 7095−7109.
(17) Park, H.; Zhao, J.; Lu, J. P. *Nano Lett.* **2006**, *6*, 916−919.
(18) Kuo, H. F.; Lien, D. H.; Hsu, W. K.; Tai, N. H.; Chang, S. C. *J. Mater. Chem.* **2007**, *17*, 3581- 3584.
(19) Silva, L. B.; Fagan, S. B.; Mota, R. *Nano Lett.* **2004**, *4*, 65−67.
(20) Peng, S.; Cho, K. *Nano Lett.* **2003**, *3*, 513−517.
(21) Maroto, A.; Balasubramanian, K.; Burghard, A.; Kern, K. *Chem. Phys. Chem.* **2007**, *8*, 220−223.
(22) Lee, C. W.; Zhang, K.; Tantang, H.; Lohani, A.; Nagahiro, T.; Tamada, K.; Chen, Y.; Mhaisalkar, S. G.; Li, L. J. *Appl. Phys. Lett.* **2007**, *91*, 103515/1−103515/3.