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CARBON MONO-OXIDE GAS SENSING PROPERTIES OF MULTI-WALLED CARBON NANOTUBES DECORATED WITH PLATINUM NANOPARTICLES BASED FILM SENSORS

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Carbon nanomaterials have been attracting a great deal of research interest in the last few years. The presented work in our article reports the fabrication of three types of multi-walled carbon nanotubes (MWCNTs) film sensors namely: as-synthesized nickel catalyzed MWNTs film sensor, MWNTs deposited with platinum (Pt) nanoparticles film sensor and MWNTs deposited with Pt nanoparticles film sensor annealed at 400^{o}C for one hour. The carbon mono-oxide (CO) gas sensing properties of all these three types of MWCNTs film sensors have been studied. A very thin layer (5 nm) of Pt nanoparticles has been deposited on this MWCNTs film. Gold electrodes have thermally been evaporated to get the characteristic pattern of MWCNTs film sensor. We found a typical response of MWCNTs gas sensor at four different concentration (200, 400, 600 and 800 ppm) of sensing gas. The resistance of fabricated MWCNTs film sensor increases with increase in the gas concentration whereas the sensitivity and responsiveness of the sensing film show a decreasing trend with increase in the concentration of CO gas. Our studies show a good response to the sensing CO gas with a fast recovery time. Dependence of conductivity on temperature has also been studied to explain the electrical properties of these MWCNTs film sensors.

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Keywords; Multi-walled carbon nanotubes, Gas sensor, CO gas, Recovery and response time, Sensitivity, Responsiveness

1. Introduction

Carbon materials with inherent nanoscale features have potential for becoming ideal components for the next generation of autonomous sensor technology. They combine excellent detection sensitivity with interesting transduction properties in a single layer of material. The sensitivity and selectivity of carbon nanomaterials can be engineered by employing different techniques both to create defects and graft functional groups to their surface in a controlled way. Carbon nanotubes (CNTs) have one-dimensional nanostructure with unique physical, chemical, thermal, mechanical, and electronic properties. After two decades of research efforts, CNTs show great promise for an amazing range of applications in nanotechnology. Carbon nanotubes (CNTs) with excellent mechanical properties which are associated with their high specific surface area and nanoscale structure that provides many sites where gases can react constitute a class of promising building blocks for fabricating chemical sensors [1-4]. Carbon nanotubes can be used as gas sensors because of possessing the high surface area, porous structure and the ability to be impressed by some toxic and flammable gases at room temperature

Potential applications of carbon nanotubes including as catalyst supports in heterogeneous catalysis, nanoprobes, molecular reinforcements in composites, displays, sensors, energy-storage media, high strength engineering fibers etc. result mainly from theirs high surface area, mechanical

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strength, chemical and thermal stability [5-7]. CNTs based sensor has attracted a lot of attention of the scientific community because all the electronic properties of CNTs are governed mainly by the outermost layer which is chemically very active and its 1D structure provides them large surface area. The sensing mechanism of a CNT differs between reactants, but it is generally known that electron accepting molecules (e.g. NO_2) and electron donating molecules (e.g. NH_3) can interact with CNTs directly or indirectly and modify its Fermi level. There are lot of commercially available sensors based on noble metals and metal oxide materials for industrial use but still more compact and efficient gas sensors are required that can be operated on low power and have better selectivity for gaseous molecules [8, 9]. This problem is circumvented by using nano sized powders, films or by depositing these particles on other nanostructures with larger surface area. In this context, carbon based nano structured materials can be highly useful due to their large surface area and high electrical conductivity. CNT gas sensors can be classified into two main categories: single aligned CNT devices and the simpler random network CNT type. In the case of a single aligned CNT, the sensors offer good sensitivity at room temperature, but the fabrication costs are high and the sensors offer limited selectivity with an irreversible response [10]. In response, metal-decorated CNT random network sensors have been researched [11, 12] to functionalize and to improve outer most walls of CNTs. These devices are formed by covering or "decorating" metal particles on the surface of the CNTs to enhance sensitivity to certain gas species compared with bare CNT networks. Furthermore, better selectivity can be obtained in sensors intended to detect natural gases because sensitivity depends strongly upon the type of metal deposited. Metal-decorated random-network CNT network sensors often display both better reversibility [13-15], and fabrication procedures are more easily scaled than the single-CNT type.

In recent years, considerable research has been focused on the development of technologies capable to decorate both SWCNTs and MWCNTs with different metals and their oxides for selectively sensitive to different gases. Therefore, workers in this field have decorated different metal nanoparticles such as palladium, gold, iridium and platinum (Pt) onto the surface of CNTs. Out of these noble metal nanoparticles, Pt has widely been used in many applications, especially as a catalyst for carbon monoxide (CO) oxidation in catalytic converters and for fuel cell technology [16-20]. Several methods have successfully been developed and practically applied, for example nano composites based on depositing Pt nanocrystals onto carbon nanotubes play an important role in fuel cell application [21-23] for fabricating electrochemical sensors [24-28] and in many others. Because of diverse set of applications, different kinds of electrochemical, chemical, and physical methods have been developed to effectively synthesize Pt/CNTs composites [29, 30].

In this research manuscript, we report on our investigation on MWCNTs deposited with Pt nanoparticles film sensor for the detection of CO gas.

2. Experimental

We have fabricated three types of sensing CNTs films namely: as-prepared CNTs film, CNTs film with a Pt layer of 5 nm deposited on it and CNTs film with a Pt layer of 5 nm annealed at 400^{o}C for one hour. The carbon nanotubes were synthesized on silicon substrate using low pressure chemical vapor deposition method. After deposition of CNTs, a thin layer (5 nm) of platinum was deposited using sputtering and this film was annealed at 400^{o}C for one hour for the attachment of Pt nanoparticles on the surface of CNTs. The morphology of these multiwalled carbon nanotubes (MWCNTs) were studied using field emission scanning electron Microscope (FESEM). We have recorded the Raman spectra of as-grown CNTs using DXR Raman Microscope (Thermo Scientific) with 532 nm laser as an excitation source of 8 mW. A specially designed gas sensing set-up was used to study the gas sensing properties of the present MWCNTs based sensor. To study the gas sensing properties of the as-prepared MWNTs films, MWNTs gas sensor was kept inside a stainless steel chamber and the resistance was measured using a Keithley 4200; I-V measurement system. An electrode pattern of gold was thermally evaporated on this MWNTs film. The sample was examined in a chamber with the detecting gases flowing through over. The mass flow controllers were used to control the concentration of detecting gas. For

measuring the gas sensing properties, MWNTs based sensor was kept inside the sample holder and probes were connected on the electrodes of MWNTs film. The system was evacuated up to 10^{-6} Torr with the help of turbo molecular pump. After attaining the required degree of vacuum, the turbo and rotary pump valves were closed and air was purged with the flow rate of 2 L/min for 5 min. The real time resistance was measured to obtain a baseline resistance. Once a baseline resistance is obtained, the detecting gas i.e. carbon monoxide with set concentration was introduced into the sample holder. The gas was purged for 1-2 minutes to measure the change in resistance with time and after the time was over, the flow of detecting gas into the sample holder was stopped and measured recovery time of the sensor. We repeated these cycles for different concentrations of carbon monoxide with respect to pure air to study the response of this MWNT sensor for detecting CO gas. The clean air reference flow time and the sample gas flow time were fixed at 2 minutes and 1-2 minutes, respectively. It should be noted that these switching intervals were selected so that the resistance change is at least 90% of the saturated value. The sensor resistance was sampled and recorded every second for subsequent analyses.

3. Results and discussion

Figs. 1(a) and (b) represent the morphology of CNTs decorated with Pt nanoparticles. The diameter of these nanotubes varies from 30-80 nm and the length of these CNTs is of the order of several tens of micrometers. It is also suggest that the nanotubes are multi-walled and the deposition of some Pt nanoparticles is also seen on the surface of the nanotube. As usual, the verification of the graphitic nature of as-grown carbon nanotubes can be done using Raman spectroscopy. Here, we have undertaken the Raman studies on as-grown nanotubes film, nanotubes deposited with platinum nanoparticles film, and nanotubes decorated with Pt nanotubes with annealing at 400^{o}C for one hour. Fig. 2 presents the Raman spectra of all the studied sensor films of MWCNTs. All of these samples show the presence of strong peak at 1580 cm^{-1} (G-band), which clearly indicates the graphitized nature [31]. In CVD grown MWCNTs normally, the D-mode (the disorder band) is located between 1330 – 1360 cm^{-1}. In our case, we have observed less intense D-band peak at 1320 cm^{-1} for all studied samples, which predicts that the less quantity of amorphous carbonaceous particles is adhered on the walls of MWCNTs. Moreover, the moderate peaks are observed at 520 cm^{-1} and 1620 cm^{-1} in the samples of nanotubes deposited with platinum nanoparticles and also to that annealed at 400^{o}C for one hour. The presence of these additional peaks in Raman spectra suggest that the platinum nanoparticles are decorated on the surface of the nanotubes.

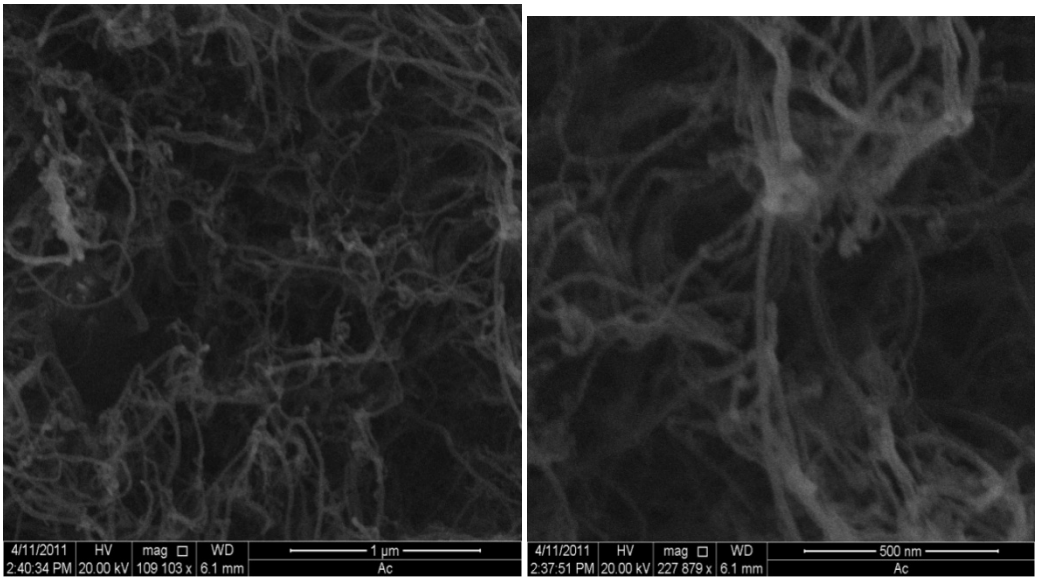

Fig. 1(a and b): FESEM images of MWCNTs deposited with platinum nanoparticles.

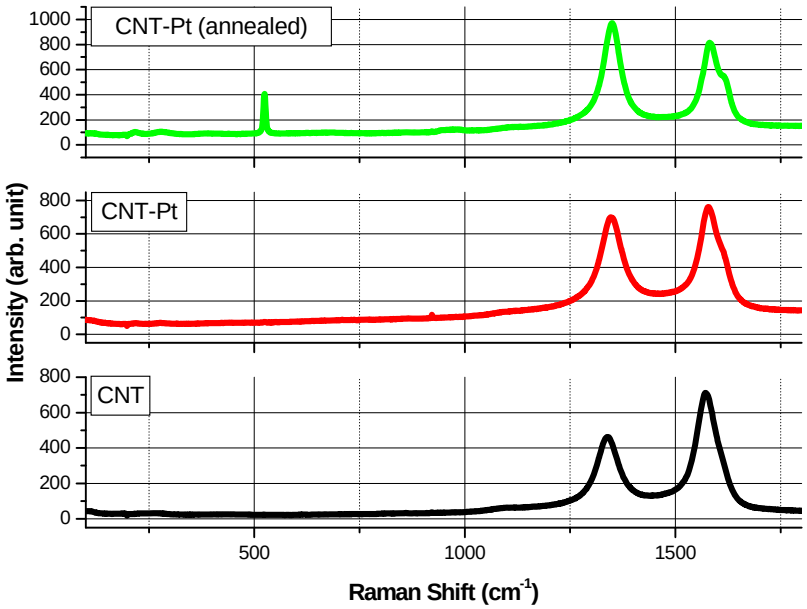

Fig. 2. Raman spectra of as-synthesized MWCNTs, MWCNTs deposited with platinum nanoparticles and MWCNTs deposited with platinum nanoparticles annealed at 400°C for 2 hours.

Typical response of this MWCNTs gas sensor in the presence of CO gas is shown in Fig. 3. It is obvious from the figure that the resistance of all the presently studied sensing materials changes after exposing to successive concentrations of CO gas. Both the response time (τ_{res}) and the recovery time (τ_{rec}) of these sensor films show overall an increasing trend for different concentration of CO gas (200, 400, 600 and 800 ppm). For the as-synthesized MWCNTs sensing film, the both τ_{res} and τ_{rec} increases from 14.18 to 23.46 and 12.55 to 14.73 seconds, respectively, with the increase in the CO concentration. Further, τ_{res} and τ_{rec} increases respectively, from 13.54 to 18.55 and 9.18 to 11.45 seconds for MWCNTs film decorated with platinum nanoparticles. It has also been noted that these values do increase from 9.82 to 19.09 seconds and 11.46 to 14.18 seconds for annealed sensing film. The calculated values of response and recovery time for different concentrations of CO are presented in Tables 1, 2 and 3. Here, it is seen that all the studied samples show fast recovery and response to the CO gas. The fast recovery time may be explained due to the low binding energy between MWCNTs and CO gases. The fast response and recovery time may also be suggested due to either the fast adsorption/desorption process of gas molecules on MWCNTs/MWCNTs decorated platinum nanoparticles or weak bonds and less partial electron transfer between MWCNTs/MWCNTs decorated platinum nanoparticles and CO molecules.

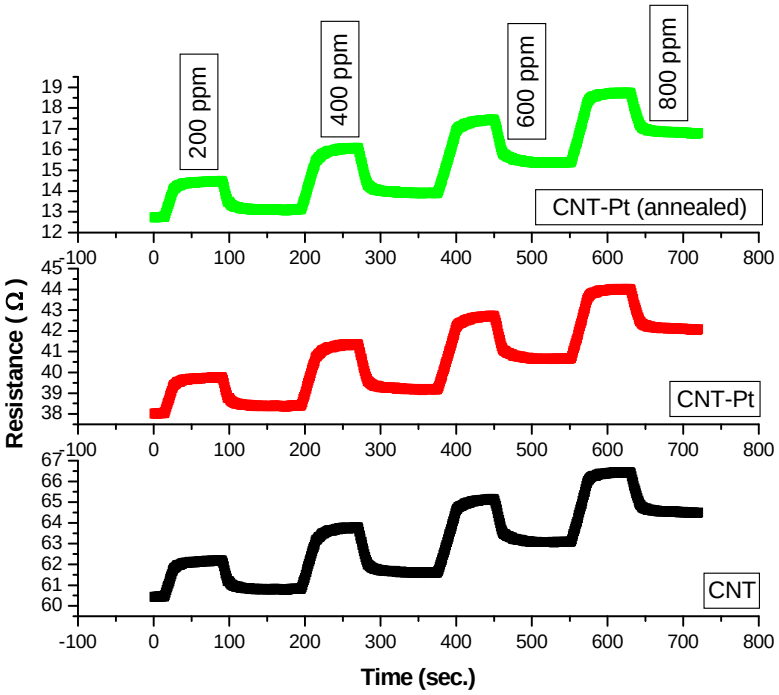

Fig. 3.Typical responses of MWCNTs film sensor, MWCNTs deposited with platinum nanoparticles film sensor and MWNTs deposited with platinum nanoparticles film sensor annealed at 400^{o}C for 1 hours for different concentration of CO gas (200, 400, 600 and 800 ppm).

The resistance of carbon nanotubes shows a significant change on CO exposure. The maximum resistance detected is 62.23 Ω at 200 ppm concentration of CO (Table 1), which is higher than the resistance measured in air (60.25 Ω). It is well known that carbon monoxide is a reducing gas and its absorption will result injection of electrons to the CNTs and reduction in the number of holes in the material. As holes are the main charge carrier for p-type semiconductor, the reduction in the number of holes will result in an increase in resistance of the sample on the exposure of CO gas.

We observed that on increasing the CO gas concentration from 200 ppm to 600 ppm, the resistance of MWNTs film sensor also increases. To evaluate the sensitivity of this MWCNTs gas sensor, we use the following relation [32]:

Sensitivity = $R_{air}/R_{gas}$where R_{air} is the sensor resistance in air and R_{gas} is the sensor resistance in the presence of a toxic species. Using above relation, we have calculated the sensitivity of these gas sensors and its variation with time for different CO gas concentration is shown in Fig. 3. It is seen that the sensitivity of MWCNTs gas sensor decreases with the increase in CO gas concentration from 200 ppm to 600 ppm. This means that the process of CNTs-hybridization reduces the gas sensitivity towards CO gas.

The responsiveness (SR) of a sensor is defined as the ratio of the resistance change due to the exposure to the test gas and the sensor's baseline resistance in air. For quantifying the performance of a given sensor, we use the following relation [32]:

$$SR = (R_{air} - R_{gas})/R_{air}$$

The responsiveness of these sensor films has been calculated using above relation at different CO concentration and the values are tabulated in Tables 1, 2 and 3. It is clear from the table that all studied MWCNTs gas sensors can detect the gas concentrations ranging from 200 ppm to 600 ppm of CO.

Table-1. Typical sensing parameters of as-synthesized MWCNTs based film sensor.

CO concentration (ppm)	**Resistance** (Ohm)	**Responsiveness** $[(R_{air} - R_{gas})/R_{air}]$ (%)	**Sensitivity** (R_{air}/R_{gas}) (%)	**Response Time** (τ_{res}) (Sec)	**Recovery Time** (τ_{rec}) (Sec)
200	62.23	2.79	97.44	14.18	12.55
400	63.77	5.26	94.87	20.72	13.08
600	65.13	7.27	92.87	26.27	14.18
800	66.51	9.08	91.07	23.46	14.73
Air	60.25	-----	-----	-----	-----

Table-2. Typical sensing parameters of MWCNTs decorated with Pt nanoparticles based film sensor.

CO concentration (ppm)	**Resistance** (Ohm)	**Responsiveness** $[(R_{air} - R_{gas})/R_{air}]$ (%)	**Sensitivity** (R_{air}/R_{gas}) (%)	**Response Time** (τ_{res}) (Sec)	**Recovery Time** (τ_{rec}) (Sec)
200	39.74	4.51	95.83	13.54	9.18
400	41.35	8.12	92.21	20.73	14.19
600	42.72	11.08	89.26	21.21	10.91
800	44.02	13.74	86.49	18.55	11.45
Air	37.76	-----	-----	-----	-----

Table-3. Typical sensing parameters of annealed MWCNTs decorated with Pt nanoparticles based film sensor.

CO concentration (ppm)	**Resistance** (Ohm)	**Responsiveness** $[(R_{air} - R_{gas})/R_{air}]$ (%)	**Sensitivity** (R_{air}/R_{gas}) (%)	**Response Time** (τ_{res}) (Sec)	**Recovery Time** (τ_{rec}) (Sec)
200	14.49	11.84	88.22	9.82	11.46
400	16.10	20.69	79.36	17.45	10.91
600	17.46	26.69	73.03	22.37	11.23
800	18.83	31.92	67.84	19.09	14.18
Air	12.51	-----	-----	-----	-----

Fig. 4 shows the variation of the responsiveness with time at different CO gas concentrations. It is found that the responsiveness increases with the increase in gas concentration from 200 ppm to 600 ppm. It is therefore, suggested that this MWCNTs sensor gives a significant response to the different concentrations of CO gas.

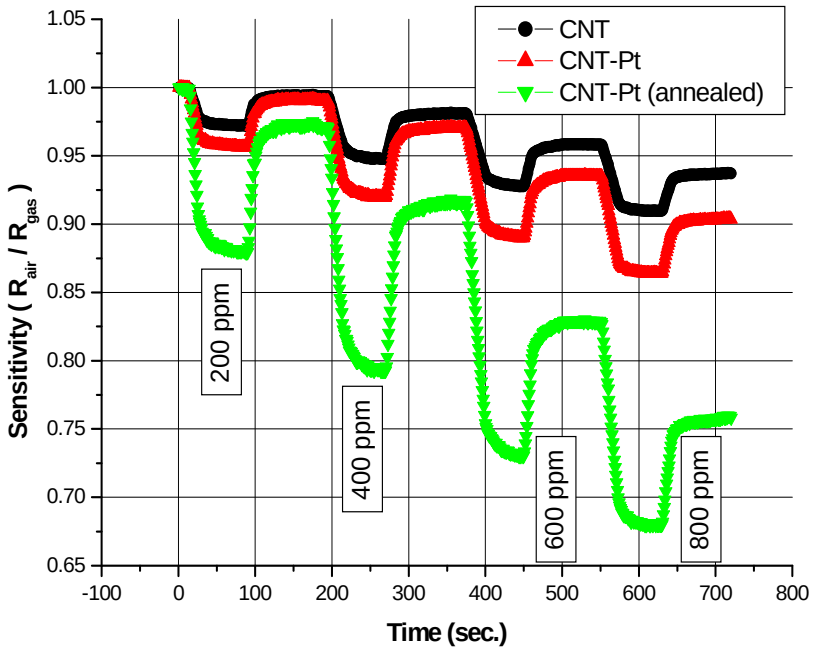

Fig. 4. Typical sensitivity of MWCNTs film sensor, MWCNTs deposited with platinum nanoparticles film sensor and MWCNTs deposited with platinum nanoparticles film sensor annealed at 400°C for 1 hours for different concentration of CO gas (200, 400, 600 and 800 ppm).

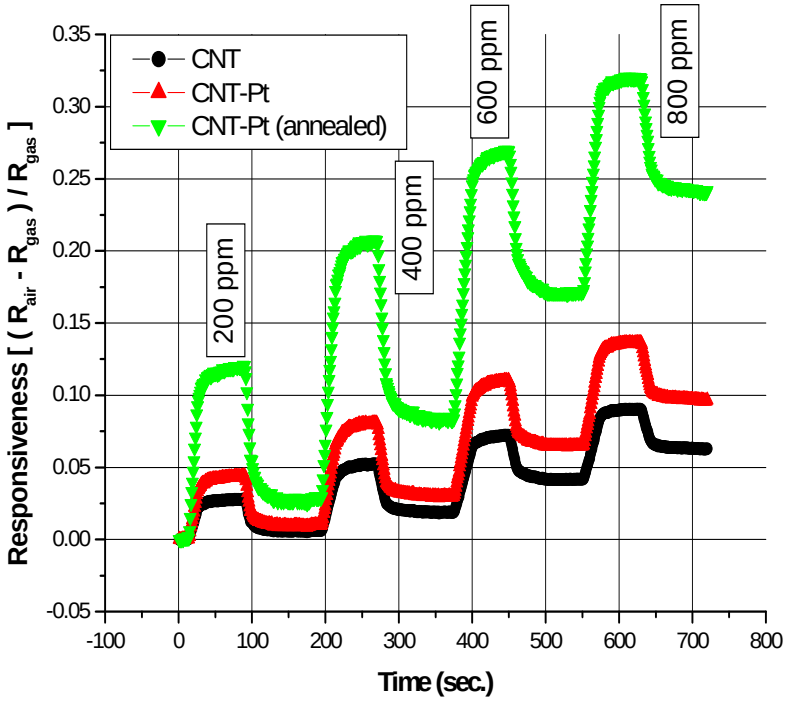

Fig. 5. Typical responsiveness of MWCNTs film sensor, MWCNTs deposited with platinum nanoparticles film sensor and MWCNTs deposited with platinum nanoparticles film sensor annealed at 400°C for 1 hours for different concentration of CO gas (200, 400, 600 and 800 ppm).

In the present system, the electrical response to the molecular adsorption in MWCNTs may be explained on the basis of two sensing mechanisms namely (i) the adsorption resulting in direct charge transfer between a donor or acceptor type of molecule and MWNTs, which lead to the shift in Fermi level in the semiconducting tubes (intra-tube modulation), tends a change in the resistance [33], (ii) the adsorption occurs in the interstitial space between MWCNTs to form an MWCNT-molecule-MWCNT junction, which results in a hopping kind of mechanism for inter-tube charge transfer between nanotubes. Therefore, an inter-tube modulation of the CNTs network may be responsible for the change in resistance. This phenomenon is common for all types of molecules and for the both metallic and the semiconducting CNTs. This type of modulation is similar to that of the interaction between semiconductor metal oxides and donor or acceptor types of molecules, showing a nonlinear (power law) response [34].

4. Conclusion

We have studied three types of MWCNTs based film sensors $i.e.$ as-synthesized MWCNTs based film sensor, MWCNTs decorated with platinum nanoparticles based film sensor and the annealed MWCNTs decorated with platinum nanoparticles based film sensor for detecting the different levels of CO gas. The typical responses of all of the studied MWCNTs gas sensors in the presence of CO gas suggest that response time and the recovery time increases with the increase in CO gas concentration. All the studied sensors depict fast response and recovery time. The fast recovery time of the sensors may be due to the fast adsorption/desorption process of gas molecules on MWCNTs. The sensitivity of the studied MWCNTs sensing films shows a decreasing trend, whereas the responsiveness increases with the increase in the CO gas concentration. It is, therefore, suggested that this MWCNTs sensor gives a significant response to the different concentrations of CO gas.

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References

[1] L. Li, G. Zhang, L. Chen, H. M. Bi, K. Y. Shi, Materials Research Bulletin **48**, 504 (2013).
[2] Z. Mahdavifar, N. Abbasi, E. Shakerzadeh, Sensors and Actuators B: Chemical **185,** 512 (2013).
[3] H. Kim, M. H. Hong, Ho W. Jang, S. J. Yoon, H. H. Park, Thin Solid Films **529**, 89 (2013).
[4] D. Shi, L. Wei, J. Wang, J. Zhao, C. Chen, D. Xu, H. Geng, Y. Zhang, Sensors and Actuators B: Chemical **177**, 370 (2013).
[5] R. H. Baughman, A. A. Zakhidov, W. A. Zakhidov, Science **297**, 787 (2002).
[6] B. I. Yakobson, R. E. Smalley, Am. Sci. **85**, 324 (1997).
[7] P. M. Ajayan, Chem. Rev. **99**, 1787 (1999).
[8] E. Llobet, Sensors and Actuators B: Chemical **179**, 32 (2013).
[9] J. S. Lee, T. J. Ha, M. H. Hong, C. S. Park, H. H. Park, Applied Surface Science **269**, 125 (2013).
[10] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, Science **287**, 622 (2000).
[11] T. Zhang, S. Mubeen, N. V. Myung, M. A. Deshusses, Nanotechnology **19**, 33 (2008).
[12] A. Goldoni, L. Petaccia, S. Lizzit, R. Larciprete, J. Phys. Condens. Matter **22**, 8984 (2010).
[13] N. V. Hieu, L. T. B. Thuy, N. D. Chien, Sens. Actuat. B **129**, 888 (2008).

[14] M. Yang, D. H. Kim, W. S. Kim, T. J. Kang, B. Y. Lee, S. Hong, Y. H. Kim, S. H. Hong, Nanotechnology **21**, 215501 (2010).
[15] G. Lu, L. E. Ocola, J. Chen, Adv. Mater. **21**, 2487 (2009).
[16] G. C. Bond and D. T. Thompson, Gold Bulletin **33**, 41 (2000).
[17] M. Kang, M. W. Song, C Ha Lee, Applied Catalysis A: General **251**,143 (2003).
[18] Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, Angewandte Chemie **48**, 60 (2009).
[19] J. Wu, A. Gross, H. Yang, Nano letters **11**,798 (2011).
[20] J. John, E.Gravel, I. N. N. Namboothiri, E. Doris, Nanotechnology Reviews **1/6**, 515 (2012).
[21] W. Li, C. Liang, J. Qiu, W. Zhou, A. Zhou, Z. Wei, G. Sun, Q. Xin, J. Physical Chemistry B **107**, 6292 (2003).
[22] H. Y. Du, C. H. Wang, H. C. Hsu, S. T. Chang, U. S. Chen, S. C. Yen, L. C. Chen, H. C. Shih, K. H. Chen, Diamond and Related Materials **17**,535 (2008).
[23] S. Ghosh and C. R. Raj, J. Phys. Chem. C **114**, 10843 (2010).
[24] C. Hu, S. Hu, Journal of Sensors **2009**, 1 (2009).
[25] X. H. Kang, Z. B. Mai, X. Y. Zou, P. X. Cai, J. Y. Mo, Talanta **74**, 879 (2008).
[26] G. Lota, K. Fic and E. Frackowiak, Energy Environ. Sci. **4**, 1592 (2011).
[27] M. G. Straver, M. Odijk, W. Olthuis, A. van den Berg, Lab Chip, **12**, 1548 (2012).
[28] W. Lian, S. Liu, J. Yu, X. Xing, J. Li, M. Cui, J. Huang, Biosensors and Bioelectronics **38**, 163 (2012).
[29] J. Chen, B. Lim, E. P. Lee, Y. Xia, Nano Today **4/1**, 81 (2009).
[30] D. Wen, X. Zou, Y. Liu, L. Shang, S. Dong, Talanta **79/5**, 1233 (2009).
[31] A. A. Al-Ghamdi, Shamshad A. Khan, Zishan H. Khan, Advanced Science Letters **16**, 377 (2012).
[32] Z. H. Khan, M. S. Ansari, N. A. Salah, A. Memic, S. Habib, M. S. Shahawi, Digest J. of Nanomaterials and Biostructures **6**, 1947 (2011).
[33] J. Zhao, A. Buldum, J. Han, J. P. Lu, Nanotechnology **13**, 195 (2002).
[34] J. Gardner, P. N. Bartlett, Electronic Nose: Principles and Applications, Oxford University Press, New York (1999).