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CHEMIRESISTIVE SENSOR BASED ON PORPHYRIN FUNCTIONALIZED SWNTs: EFFECT OF SPIN COATING PARAMETERS

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Abstract: A low cost, sensitive and reproducible room temperature sensor for the detection of toluene has been demonstrated with tetraphenyl porphyrin functionalized single wall carbon nanotubes. Non-covalent route was adapted for the functionalization. Field emission scanning electron microscopy was carried out to reveal the morphological impression of the functionalized structures. Electrical behaviour of the functionalized single wall carbon nanotubes was studied as a function of porphyrin coating thickness. I/V studies confirmed the formation of an effective charge transfer complex between porphyrin and SWNTs. The functionalized structures were successfully characterized as room temperature chemiresistive toluene sensors. Sensing characteristics of all the fabricated sensors were carried out in toluene atmosphere in true dynamic mode. Sensing characteristics were recorded in the concentration window of 50 ppm to 150 ppm of toluene. Observations well revealed that thickness of the functionalizing entity has a profound role in controlling the sensing behaviour. It could be well inferred from the observations that in spite of not being a conventional functionalization technique, spin coating, by dint of its simplicity and ease of reproducibility, could be highly instrumental in defining optimized sensor characteristics.

Keywords: SWNTs, TPP, Toluene, Spin Coating.

1. INTRODUCTION

Gas sensors, undoubtedly, constitute a research area of paramount interest due to its scientific, technical, medical and market potential. Continuum of research efforts are continuously under scientific scanners to obtain gas sensors with specific tailor-made characteristics and as an obvious fact, very few sensors could have been reported till date that accumulate apex of the all requisite qualities of an ideal sensor. A broad effort on possible classification of research on gas sensors find two areas of highest interest- (i) pursuit of novel/smart sensing materials and (ii) efficient synthesis and/or modification techniques to employ the sensing material at their highest possible efficiency. Till date, different techniques such as electrochemical deposition [1], sputtering [2], spray pyrolysis [3], spin coating [4], chemical deposition [5] etc. have been employed for gas sensor fabrication. Recently, spin coating technique has been found to gain enormous preference due to ease in experimentation and high rate mass production.

It was observed that the thickness of spin coated film plays crucial role in deciding electrical and sensing characteristics of sensor [4, 6]. Efforts were made in this direction by several researchers. N. Kakati et al. [4] had developed ZnO thin films for the detection of acetone vapours in the 100 ppm to 1000 ppm concentration range where the authors have concluded that morphology of the film was totally dependent upon its thickness. As thickness increases structure becomes more porous. More porous structure also harms the sensing characteristics of the sensor. Therefore, in order to form efficient sensor, thickness control seems to be essential. K. Mukherjee et al. [6] fabricated $Mg_{0.5}Zn_{0.5}Fe_2O_4$ based sensor for hydrogen in 50 ppm to 1000 ppm concentration range. Here, the authors have demonstrated that thickness of the spin coated film decides the affection of sensor towards analytes.

In the present communication, the authors have employed spin coating technique for non-covalent functionalization of single wall carbon nanotubes (SWNTs) by tetra phenyl porphyrin (TPP). Non-covalent functionalization of SWNTs, a well established supra-molecular approach, is of high benefit for sensing applications because- (i) this technique aids to retain the surface activity of SWNTs and (ii) due to weak forces of interaction present e.g Van-der Wall's attraction, adaptive wrapping , there is formation of extended π delocalization at the interfacial sites that facilities facile charge transfer.

Our research group has successfully demonstrated the potential of porphyrin/metalloporphyrin functionalized SWNTs for real time monitoring of the volatile organic compounds (VOCs) at room temperature [7-9]. VOCs are ubiquitously present in the air we inhale and the adverse health effects are often too slow for early medical diagnosis. In the chemiresistive modality of operation, SWNTs act as transduction element where as porphyrins play central role in sensing by showing affinity towards the target VOCs. Therefore, in order to get the optimum sensing responses, role of each sensing material should be well exploited in the sensing mechanism so that the individual superior characteristics are not suppressed. From this point of view, the coating thickness of the porphyrin layer is matter of crucial interest since an optimum thickness can ensure sensitive detection of the analyte with minimal surface adsorption and concurrent transfer of the effects of analyte/porphyrin interaction to the subsequent SWNTs channel. Therefore, suitable control methodology for defining optimal thickness for the porphyrin layer [10] is highly warranted and very few efforts in this line of investigation were reported till date.

In the present report, findings based on comparative sensing study of TPP functionalized SWNTs as a function of the thickness of TPP layer are presented. Initially, SWNTs were spin casted (2000 rpm) from NNDMF-SWNTs suspension (ultrasonicated; 0.50 mg/20ml) to form a network of SWNTs between a sub mm apart thermally deposited Al fingertips on glass substrate [11]. Spin coated SWNTs network were annealed in nitrogen atmosphere for 90 min. For functionalization, a suspension (0.1mM) of TPP (in NN-DMF) was spin-coated onto the SWNTs at three different spin speeds (1500rpm, 2000rpm and 2500rpm; each for 25s) to obtain various thickness of SWNTs coverage. All syntheses and measurements were carried out under ambient condition unless stated otherwise.

In due course of discussions to follow, fabricated sensor devices are named as follows:

Table 1 *Nomenclature of fabricated Sensors*

Devices with TPP deposition speed	Device name
1500 rpm	D_1
2000 rpm	D_2
2500 rpm	D_3

2. Results and Discussion

2.1 Field Emission Scanning Electron Microscopy (FESEM): Morphological Investigation

Field emission scanning electron microscopic (FESEM) images of the devices were recorded with Hitachi S-4800 field emission electron microscope. Figure 1 shows the FESEM image of the device D_2. After functionalization with porphyrin at 2000 rpm spin, average increase of ~33 nm in diameter could be observed in comparison to unfunctionalized SWNTs. For the device D_1 (data not shown) coverage of porphyrin over SWNT is maximum whereas, in case of device D_3 (data not shown) minimal layer of porphyrin was observed.

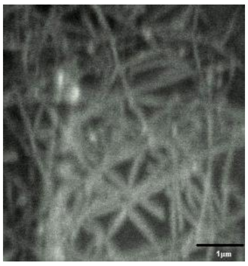

Fig. 1 *FESEM image of the sensor device D_2*

2.2 Current Voltage (I-V) Characteristics:

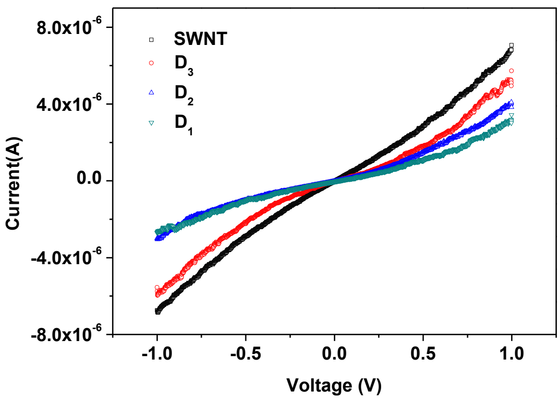

Fig. 2 *Current-Voltage Characteristics of the Fabricated Sensors*

Current-voltage (I-V) characteristics were studied with electrochemical workstation CHI 660C instrument by applying linear sweep voltammetry technique (-1V to 1V). Coating of TPP over the

SWNTs has resulted in decrease in current level of the device which confirms that there is probable electron transfer from TPP to the p-type SWNTs [12]. For highest spin speed of TPP on SWNTs network (device D_3), current is higher than its counterparts (devices D_1 and D_3). Also, the device current goes on decreasing as speed decreases (Fig. 2). Such observation might be interpreted in the manner that at lower spin speed, the effective viscous drag of the porphyrin suspension resulted in thicker TPP layer on the SWNTs that effected higher electron donation from porphyrin [13]. At highest spin speed, as reflected from the I-V characteristics, the electron donation from porphyrin is lowest that might be indicative to the fact that at highest spin speed the coating of SWNTs is not efficient. Therefore, from above findings it can be concluded that increase in spin speed would result in optimization of porphyrin thickness over the SWNTs.

2.3 Chemiresistive Sensing Characteristics:

Sensing characteristics of the fabricated sensors were carried out in chemiresistive sensing modality. Electrical contacts from the Al fingertip pads were created by silver paste and subsequent drying in ambient atmosphere. Electrical connections were finally established with PC controlled source-measure unit (Keithley 2400). The sensors were kept in a quartz flow-cell (vol. 08 cc c.a.) that allows taking out required electrical connections. Before going for sensing measurement, dry air was exposed upon the sensor in order to achieve steady base line. Various concentrations of toluene (50 ppm, 100ppm and 150ppm) were prepared by diluting it in dry air. To control the flow of analyte and dry air, mass flow controllers (ALICAT MCS200) were used. A fixed 10 μA current was applied to the sensor and consequent changes in potential due to change in analyte concentration were recorded [8]. Changes in resistances were finally estimated by applying ohm's law.

Figure 3 shows the histogram of normalized changes in resistances (=$\Delta R/R_o$; $\Delta R= R- R_o$ where R= sensor resistance at certain analyte concentration, R_o = initial/ baseline Resistance of the sensor) of the fabricated sensors towards 50 ppm, 100 ppm and 150 ppm concentrations of toluene. Results reflect observations of more than 3 devices in each case. The observations allow to infer that the device D_2 shows best sensing characteristics.

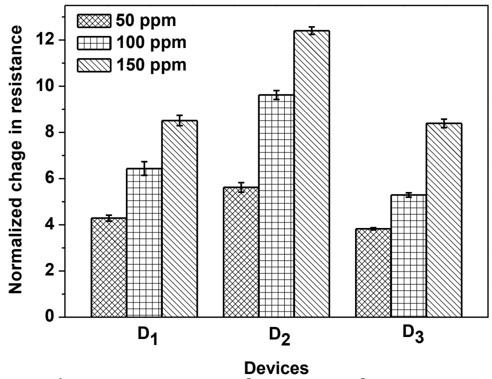

Fig. 3 *Histogram showing Toluene Sensing of Fabricated Sensor*

Figure 4 shows calibration plots of the validated sensors that certainly shows the better sensing performance of the D_2 device than D_1 and D_3. The error analysis clearly indicates that the fabrication of the sensors has resulted significant repeatability in performance.

From figure 3 and 4, it is concluded that sensing capability of the sensors was in the following order:

$D_2 > D_1 > D_3$

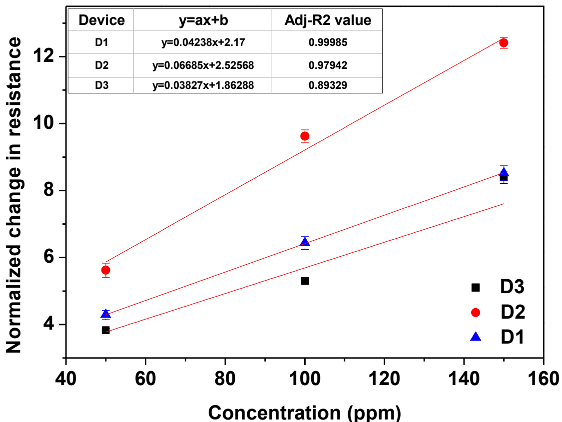

Fig. 4 *Sensitivity characteristics of fabricated devices towards various concentrations of toluene*

Such observations allow inferring that an optimum coating thickness of TPP layer has resulted in best sensing performance that might be due to most effective π delocalization at the SWNTs-TPP interface. The most insignificant performance of D_3 puts an obvious question about the role of TPP layer in that case. Further investigation is required to have further insight of the physical situation.

3. Conclusions

A low cost, efficient sensor was formed for the detection of toluene well below its PEL (200 ppm). Supramolecular approach for functionalization of SWNTs has been employed since this allows retaining the surface activity of SWNTs. Non-covalent functionalization of SWNTs, therefore, is a sector of paramount technological importance. Morphological studies of the fabricated devices show the physical coverage of porphyrin over the SWNTs depends on the spin speed. I-V studies clear that as spin speed increases, porphyrin layers thickness decreases which results in lesser electron donation, thereby allowing a control over device conductance. Sensing studies have revealed that efficient sensing performance needs an optimum thickness of the TPP layer. Best sensing results were obtained for device that was functionalized at a spin speed of 2000 rpm. Thus, it could be well concluded that thickness of functionalization entity is an important factor in SWNTs based functionalized structures and the same could be effectively tuned by varying spin coating parameters to obtain optimum sensing performance.

REFERENCES

[1] A. Ghosh, B. Bhushan Show, S. Ghosh, N. Mukherjee, G. Bhattacharya, S. K. Datta and A. Mondal, *"Electrochemical Synthesis of p-CuO Thin Films and Development of a p-CuO/n-ZnO Heterojunction and Its Application as a Selective Gas Sensor"*, RSC Adv. 4 (2014) 51569.

[2] M. Dwivedi, J. Bhargava, A. Sharma, V. Vyas, *"CO Sensor Using ZnO Thin Film Derived by RF Magnetron Sputtering Technique"* Sensors 14 (2014) 1577.

[3] M. M. Abdullah, M. H. Suhail, S. I. Abbas, *"Fabrication and Testing of SnO_2 Thin Films as a Gas Sensor"* Archives of Applied Science Research, 4 (2012), 1279.

[4] N. Kakati, S. H. Jee, S. H. Kim, J. Y. Oh, Y. S. Yoon *"Thickness Dependency of Sol-Gel Derived ZnO Thin Flms on Gas Sensing Behaviors",* Thin Solid Films 519 (2010) 494.

[5] S. Roy, H.Saha, C. K. Sarkar, "*High Sensitivity Methane Sensor By Chemically Deposited Nanocrystalline Zno Thin Film*" International Journal on Smart Sensing and Intelligent Systems, 3(2010) 605.

[6] K. Mukherjee, S.B. Majumder, *"Hydrogen Sensing Characteristics of NanocrystallineMg0.5Zn0.5Fe2O4 thin film: Effect of film thickness and operating temperature*" i n t e r n a t i o n a l journal o f hydrogen energy 3 9 (2 0 1 4) 1 1 8 5.

[7] M. D. Shirsat, T, Sarkar, J. Kakoullis, N. V. Myung, et al. *"Porphyrin-Functionalized Single-Walled Carbon Nanotube Chemiresistive Sensor Arrays for VOCs"* J. Phys. Chem. C, 116 (2012) 3845.

[8] A. Rushi, K Datta, P. Ghosh, A. Mulchandani, and M. D. Shirsat, *"Iron Tetraphenyl Porphyrin Functionalized Single Walled Carbon Nanotubes for Detection of Benzene"* Mater. Lett. 96 (2013) 38.

[9] A. Rushi, K Datta, P. Ghosh, A. Mulchandani, and M. D. Shirsat, *"Selective Discrimination among Benzene, Toluene, and Xylene: Probing Metalloporphyrin-Functionalized Single-Walled Carbon Nanotube-Based Field Effect Transistors"* J. Phys. Chem. C 118 (2014) 24034.

[10] T Sarkar, S Srinives, S Sarkar, RC Haddon, A Mulchandani, *"Single-Walled Carbon Nanotube-Poly (Porphyrin) Hybrid for Volatile Organic Compounds Detection*" J. Phys. Chem. C 118 (2014) 1602-1610

[11] A. Rushi, K. Datta, P. Ghosh and M. D. Shirsat, *"Sensitive Detection of Methyl Ethyl Ketone at Room Temperature"* National Conference on Upcoming Trends in Chemical Science UTCS (2013) 104-106.

[12] D. R. Kauffman, O. Kuzmych, A. Star, *"Interactions between Single-Walled Carbon Nanotubes and Tetraphenyl Metalloporphyrins: Correlation between Spectroscopic and FET Measurements"* J. Phys. Chem. C 111 (2007) 3539.

[13] http://edoc.unibas.ch/518/1/DissB_7698.pdf