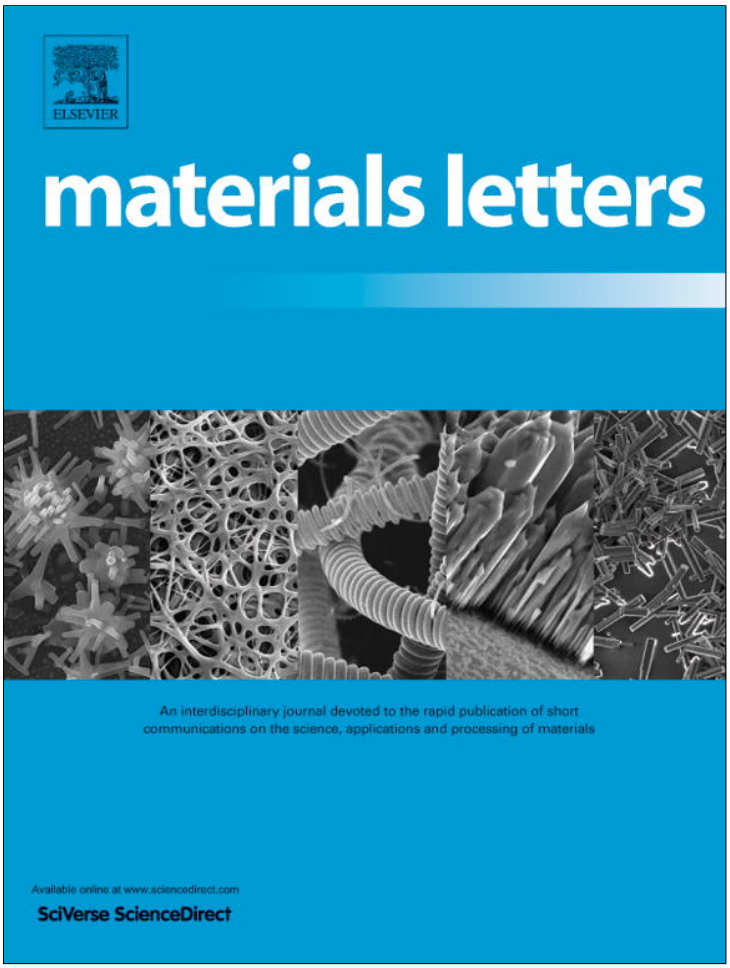

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Iron tetraphenyl porphyrin functionalized single wall carbon nanotubes for the detection of benzene

A. Rushi [a], K. Datta [a], P. Ghosh [a], A. Mulchandani [b], M.D. Shirsat [a,*]

[a] Intelligent Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, MS, India
[b] Department of Chemical and Environmental Engineering, University of California, Riverside, 900 University Avenue, Riverside, CA 92521, USA

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ABSTRACT

Non-covalently functionalized SWNTs with iron tetraphenyl porphyrin (FeTPP) were employed for detection of benzene in a sensing window of 1–25 ppm at room temperature. Formation of the SWNT–FeTPP complex was confirmed by morphological, electrical and field effect studies that revealed an electron donating nature of porphyrin. The SWNT–FeTPP sensor showed an average sensitivity of 62% and excellent linearity for validated window of concentration. The typical response and recovery time of the sensor were recorded to be in the order of seconds. In comparison to the sensing behavior of SWNT–TPP (tetraphenyl porphyrin) sensor, the SWNT–FeTPP sensor exhibited a superior sensing. The central metal ion in case of FeTPP functionalized sensor is found to be instrumental in deciding the sensing behavior.

1. Introduction

Exponential increase in unplanned urbanization and industrialization across the globe has resulted in deterioration of quality of air, water and land. Increasing number of motor vehicles, power generation units, refineries, etc. are threats to the environment due to the high rising factors like fuel combustion and untreated wastes. These anthropogenic sources are always under scan and regulations have been framed to control the roots, however, the regulation of biological generation of pollutants is another severe point of concern. Among the large spectrum of atmospheric pollutants, volatile organic compounds (VOCs) are perhaps the worst menacing outcomes of this combined effect of natural and artificial sources since the concentrations of the presence of VOCs are usually low and the health effects are mostly slow to be detected at an early stage.

VOCs exist abundantly in nature, yet, mostly neglected in our day to day life. Several VOCs are having very low PEL (0.1 ppm—acrolein, 1 ppm—benzene, 2 ppm—acrylic acid, etc.) and more pronounced are the long term exposure effects [1,2]. Among the large spectrum of VOCs, benzene has been identified as one of the most dangerous emissions [3] due to its low PEL, slow carcinogenic effects and active role in diseases like bone marrow abnormalities, acute myeloid leukemia (AML), acute lymphoblastic leukemia (ALL), chronic myeloid leukemia (CML) [4–6], etc. A colorless odorant in nature, benzene is a common ingredient of motor vehicle exhausts, glues, paints, detergents, furniture wax, tobacco smoke, etc. Since these root causes are always in ascending mode, there should be sensitive, reliable and stable means for detection of benzene. Reliable sensing of benzene has always been a challenge for researchers due to its highly stabilized and slowly-reactive nature [7]. Reported sensors for benzene are mostly in the form of thin films [4,8] and suffer from individual shortfalls like lower detection limit [8], high operating temperature [3,9,10], low response [11], low recovery [4], and high end instrumentation [12].

Comparatively a young class of macromolecular materials, e.g. porphyrins and metalloporphyrins (MPs), has shown highly encouraging results for VOCs sensing. Several researchers have shown successful sensing of benzene at low concentration of occurrence with MPs [13–15]. However, most of these sensing has been carried with QCMB assemblies [14] whereas study of electrical responses of MPs has mostly been neglected due to their low electrical conductivity [16]. Surface functionalization of high electroactive materials with MPs can be a straight forward solution to this problem. Recently, surface functionalization of SWNTs by MPs has been successfully demonstrated for selective sensing of VOCs by Shirsat et al. [16]. Due to the planer structure of porphyrins, they can be well employed for non-covalent functionalization of SWNTs to retain the surface activity of SWNTs and successful formation of charge transfer complexes with SWNT–MP system is well reported [17–19].

In the present investigation, authors have fabricated a facile chemiresistive sensor by non-covalent functionalization of SWNTs with iron tetraphenyl porphyrin (FeTPP). The sensor has

* Corresponding author. Tel.: +91 240 2403386; fax: +91 240 2400204.
E-mail addresses: mdshirsat@gmail.com, mds_bamu@yahoo.co.in (M.D. Shirsat).

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exhibited successful sensing of benzene at low order of concentration (1–25 ppm). An excellent recovery characteristic and high operational stability of the sensor makes it potent for practical applications. Finally, to investigate any possible role of the central metal ion present in FeTPP, sensors fabricated with SWNTs–TPP was also validated and observations have been rationalized.

2. Experimental

The backbone of the sensor was constituted of aligned SWNTs between photolithographically defined Au microelectrodes (3 μm apart) onto surface of an oxidized silicon substrate (P^+ type; 300 nm oxide layer). The details of fabrication were reported elsewhere [20]. SWNTs solution was prepared by dissolving 0.41 mg carboxylated SWNTs (SWNT-COOH; Nanoshel LLC, WILMINGTON DE, USA) in 20 ml of N, N-dimethylformamide (DMF; Rankem, India) by ultrasonication (90 min). To eliminate further agglomerations, the SWNT solution was centrifuged at 15,000 rpm (90 min). To align the SWNTs, a 0.2 μl drop of SWNT suspension was dispensed between two microelectrodes and subjected to sinusoidal signal (1.5 $V_{p\text{-}p}$, 4 MHz). By varying duration of signal application, desirable initial resistance of the fabricated devices was achieved [21]. The devices were dried under nitrogen atmosphere and finally annealed (300 °C; 5% H_2 in N_2; 60 min) for better SWNT-Au electrode contacts. The aligned SWNTs were non-covalently functionalized by iron tetraphenyl porphyrin (FeTPP) and tetraphenyl porphyrin (TPP) by drop casting respective porphyrin solutions onto aligned SWNTs. The solutions (0.1 mM) were prepared by dissolving FeTPP and TPP respectively in DMF followed by continuous stirring at room temperature for 30 min.

3. Characterizations

Scanning electron microscopy images of the fabricated device was recorded by HITACHI S4800 field emission scanning electron microscope (FESEM). CHI 660C electrochemical workstation (CH Instruments; Texas, USA) was used for the studying the current–voltage (*I–V*) characteristic by applying the Linear Sweep Voltametry technique (−1 to +1 V; 10 mV/s). FET characteristics were carried in a back gate configuration with a source measure unit (KEITHLEY 2400) attached with programmable power supply (PPD3003-S; Aplab, India). Gate potential V_{GS} was swept from −40 V to +40 V and drain source voltage V_{DS} was kept constant (1 V). Chemiresistive sensing of the sensors at room temperature was carried out in a custom built system where the wire-bonded chip was isolated in a flow cell (quartz c.a. 8 cc by volume) [21]. After exposing to zero air (98.5%; 60 min) for achieving a steady baseline, the sensor was exposed to various concentrations of benzene diluted in zero air (>98.5%) in successive cycles. Mass flow controllers (ALICAT Scientific Inc., MC200) were used to control the flow of both zero air and benzene. A constant current of (10 μA; DC) was applied to the sensor and consequent changes in potential as a function of various concentration of benzene was recorded by a PC controlled source-measure unit (KEITHLEY 2400).

4. Results and discussion

Field emission scanning electron microscopy: Fig. 1 shows the FESEM images of bare and FeTPP functionalized SWNTs. A comparative look ensures that after functionalization the average diameter of functionalized SWNTs has enhanced by c.a 30–35 nm than bare SWNTs. The coating seems to be uniform throughout.

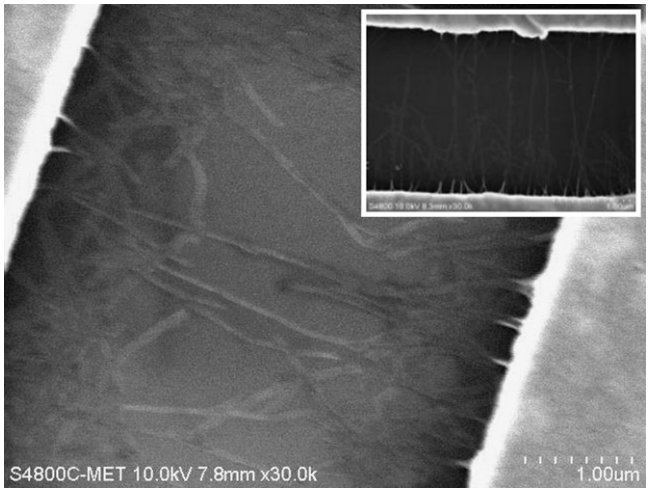

Fig. 1. FESEM images of FeTPP functionalized SWNTs (inset) bare SWNTs.

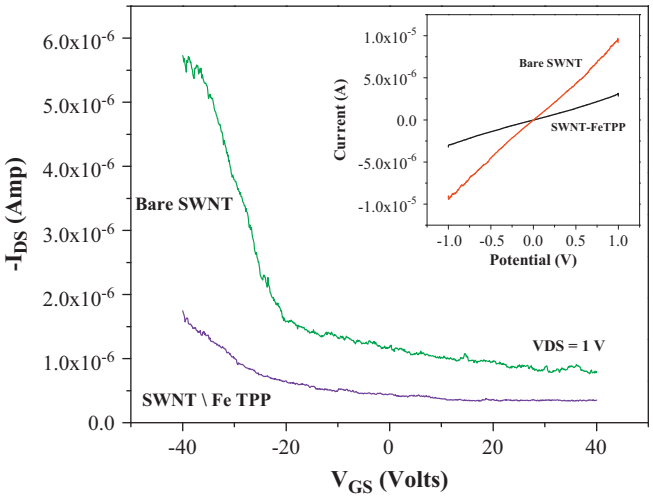

Fig. 2. Transfer characteristics bare and FeTPP functionalized SWNTs (inset) *I–V* characteristics.

I–V and FET measurement: Both the *I–V* and FET studies (Fig. 2) confirm the formation of an efficient charge transfer complex between FeTPP and SWNTs which may be attributed to planer π–π interactions between FeTPP and SWNTs [19]. *I–V* characteristics reveal typical 'S' nature for bare and functionalized SWNTs indicating formation of metal semiconductor contacts. Further, it could be observed that SWNTs–FeTPP hybrid exhibits a lower conductivity than SWNTs in pristine. Since SWNTs are inherently *p*-type [19], such observations lead to infer the electron donor role of FeTPPs. Similarly, the transfer characteristics reveal that drain current (I_{DS}) has decreased for SWNT–FeTPP complex accompanied with a negative shift of threshold voltage. It can be well apprehended that due to donation of electrons from FeTPPs to SWNTs, as discussed earlier, a lower drain current and decrease in threshold voltage was recorded. The hole concentration was reduced by a factor of c.a. $71.95 \times 10^{12}\ cm^{-1}$ for SWNT–FeTTP hybrid than pristine SWNTs while the mobilities were calculated to be $7.8 \times 10^{-2}\ cm^2\ V^{-1}\ s^{-1}$ and $30.4 \times 10^{-2}\ cm^2\ V^{-1}\ s^{-1}$ respectively [22].

Sensing behavior: Fig. 3. shows percentage changes in normalized resistance ($\Delta R/R_0$; ΔR—change in resistance and R_0—baseline resistance) of the SWNT–FeTPP sensor for various concentrations of benzene (from 1 ppm to 5 ppm). Upon exposure to benzene, the sensor showed a steep increase in resistance even at PEL

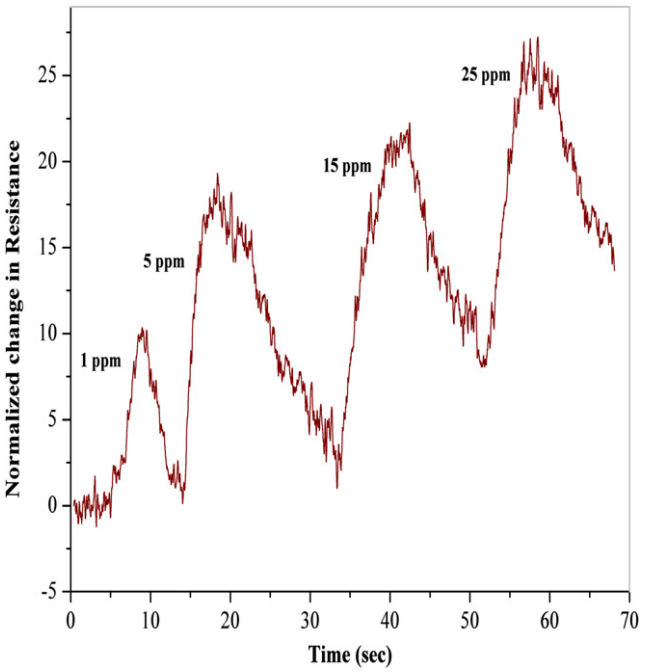

Fig. 3. Chemiresistive sensing of benzene with SWNT–FeTPP sensor.

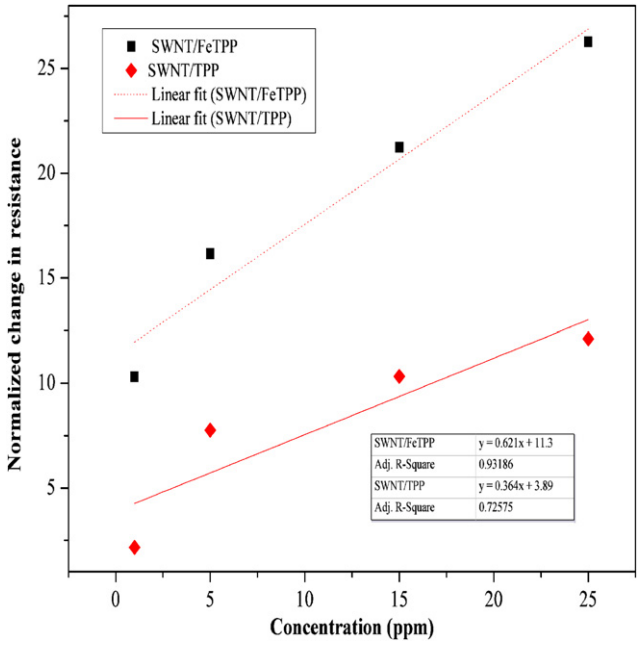

Fig. 4. Comparative performance of SWNT–FeTPP and SWNT–TPP sensor.

concentration (1 ppm) and the changes were reversible on exposure back to zero air throughout the entire window. Most encouragingly, at lower concentrations (from 1 ppm and 5 ppm), the sensor showed excellent recovery characteristic (c.a. $>90\%$). However, for higher course of concentrations, saturation in the sensing behavior was evident. Response time and recovery time of the sensor were recorded to be within c.a. from 4 s. (1 ppm) to 8 s (25 ppm). To probe if the central metal ion (Fe) in SWNT–FeTPP sensor has any significant role in sensing, a SWNT–TPP sensor was exposed to benzene under similar experimental conditions. The comparison of performances of the two sensors has been depicted in Fig. 4. The sensitivity and linearity of the FeTPP sensor (62%; $R^2=0.93$ respectively) is evidently better than the SWNT–TPP (36%; $R^2=0.72$ respectively) as reflected from the linear fit for the sensitivities at various concentrations (The sensitivity values were estimated from the slopes of the linear fit equations as provided in Fig. 4.). Exposure of benzene to the *p*-type SWNT–FeTPP sensor decreases the carrier concentration (as increase in resistance has been observed) due to shifting of valance band away from Fermi level [16] when electrons were donated to the SWNT conduction backbone by benzene [23]. Thus, the better sensing performance of the SWNT–FeTPP sensor may be attributed to the fact that transition elements (in our case Fe) are capable of accepting electrons due to their high positive charge density and partially vacant *d*-orbital. A 4% decrease in the steady state initial resistance of the sensor was recorded after 90 days (data not shown) that suggests a good operational stability of the sensor for a long duration.

5. Conclusion

In the present investigation, non-covalent functionalization of SWNTs by metalloporphyrins was found to be an excellent route for sensing of organic pollutants. The fabricated SWNT–FeTPP sensor has shown highly encouraging results for sensing of benzene. The formation of the charge transfer complex between SWNT and FeTPP were ensured by structural (FESEM) as well as electrical (I–V, FET) characterizations. Successful sensing of benzene was observed in the sensing window from 1 ppm to 25 ppm in chemiresistive modality. Electron donor nature of benzene was revealed by the sensing behavior. A behavioral comparison between SWNT–FeTPP and SWNT–TPP sensor shows that the central metal ion (Fe) plays a crucial role in enhancing the performance of the sensor. The findings have been rationalized in the manner that transition metal centers in metalloporphyrins may be important in deciding the electron donor/acceptor mechanism. Since we have not undertaken the selectivity related study for other organic analytes, further investigations are required to see if such properties can be explored for selective sensing of the same.

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