

Metal-tetraphenylporphyrin functionalized carbon nanotube composites as sensor for benzene, toluene and xylene vapors

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ABSTRACT

A process for non-covalent functionalization of multi-walled carbon nanotubes with metal-tetraphenylporphyrins is reported in this paper. The TEM and SEM images and FTIR results show that the nano-sized clusters of aggregated metal-tetraphenyl porphyrin molecules get attached and anchor the surface of carbon nanotubes. We have utilized the prepared nano-composites to fabricate very fast and sensitive sensors for detection of benzene, toluene and xylene in vapor form. The sensors made from cobalt-, and copper-tetraphenylporphyrins functionalized multi-walled carbon nanotubes having resistivity in the kilo-ohms range show response and recovery times of few seconds. However, the response and recovery times and change in resistance are strongly dependent on the type of metal-porphyrin and the chemical vapors. With the help of principal component analysis and other statistical techniques, these sensors can be used in sensor arrays to identify the specific chemicals in vapor form. The nano-composite sensors are easy to fabricate, portable, low cost, reversible, stable and very fast for detection of benzene, toluene and xylene chemicals in the vapor form. Copyright © 2014 VBRI press.

Keywords: Porphyrin functionalized carbon nanotubes; chemical vapor sensors; carbon nanotube based sensors; BTX sensor.



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include studies on metallo-porphyrins and phthalocyanines using laser based techniques, chemical vapor sensor devices based on functionalized carbon nanotubes and temperature sensors. He has more than 125 research papers published in international journals and five patents to his credit.

Introduction

Benzene, toluene and xylene commonly referred as BTX chemicals have similar chemical composition but possess distinct properties. They are extensively used in petrochemical, polymer, plastic and rubber industries. The automotive exhaust, fossil-fuel burning and tobacco smoke also contain significant amount of these chemicals. All these chemicals, especially benzene, are carcinogenic, pose a serious health hazard and contribute to environmental pollution [1,2]. Because of acute toxicities of BTX compounds, there is a need to develop sensitive, reliable, fast and portable devices for monitoring trace levels of these chemicals in environment, refineries and industries. Many techniques have been employed for detection of BTX chemicals like electronic nose [3], chromatography [4,5], electrochemical [6] and optical waveguide based sensors [7,8]. These devices have high sensitivity and selectivity. However, technical problems lie on operating some of these device systems while others have bulky structure and high cost of fabrication [4,5,7]. The UV-visible spectroscopic technique has also been tried [9,10] but the overlapping absorption in the UV region complicates the selective detection of these compounds. Some workers have also utilized metal-porphyrin thin films as sensing materials for different analytes [11-13] with limited success due to very high resistivity of the films. There is therefore a great

demand for alternate sensing devices which are reliable, sensitive, selective and portable for detection of BTX compounds.

The nanomaterial based devices offer an interesting alternative by exploiting their unique properties for various sensing applications. Out of many nanomaterials, carbon nanotubes (CNTs) and graphene have emerged as potential candidates for application as sensors for various analytes because of their unique electronic properties, large surface to volume ratio and high conductivity. Some devices have been reported using pristine multiwall carbon nanotubes (MWNTs) as sensors [14] but they respond to many type of compounds and lack selectivity. This drawback of pristine MWNTs can be overcome via surface modifications and grafting of MWNTs with different functional groups to improve sensitivity and to tailor selectivity towards specific analytes. In this direction, chemiresistive sensors based on MWNTs decorated with different noble metals for detection of some VOC gases [15-18], tetrafluorohydroquinone functionalized CNTs [19] for formaldehyde, and Fe-TPP functionalized MWNTs for benzene [20] have been reported. Recently, the authors [21] have demonstrated fabrication of a very selective sensor device made from metal-phthalocyanine (M-Pc) functionalized MWNTs for detection of H₂O₂ in the vapor form. Penza et al. [22, 23] have utilized surface modified MWNTs with different metal-porphyrins and their derivatives as functional materials for detection of few volatile compounds (NO_x, SO₂, alcohols, amines, aromatics and ketones). However, comparative study of the sensing capabilities and selectivity aspect of different M-TPP functionalized MWNTs composite materials for benzene, xylene and toluene, the three most notable pollutants and carcinogenic compounds, has not been reported.

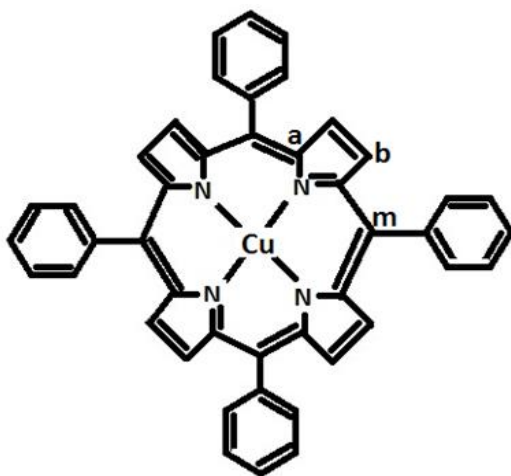


Fig. 1. Molecular structure and atomic numbering for copper-tetraphenylporphyrin.

A comparatively new class of compounds called porphyrins and phthalocyanines having extended π -electronic network have emerged as very attractive functional groups possessing multiple recognition properties. The adsorption and reactivity of analytes with metal-porphyrin derivatives can be tuned by selecting different metals at the centre and / or substituents at the porphyrin periphery which can provide selectivity to the

sensors made from such materials. Thin films of many metalloporphyrins and phthalocyanines have been utilized in mass and optical transducer systems but not as sensors electrical conductivity changes due to their very poor electrical conductivity. However, surface functionalization of MWNTs with metal-porphyrins has been demonstrated for sensing of many volatile organic compounds [20,23] as it is possible to manipulate charge transfer when metalloporphyrins are combined with MWNTs.

Structure of a typical metal-tetraphenylporphyrin is shown in **Fig. 1**. In spite of large number of studies [15-23], there is a shortage of fast, reliable and portable devices which work at normal temperature for detection of chemicals in the vapor form. We have therefore undertaken systematic studies on detection of some hazardous chemicals in vapor form utilizing the metal-porphyrin functionalized MWNTs as sensing materials.

In the present work, we report preparation of composites of different M-TPP functionalized MWNTs by blending and ultrasonification of MWNTs with M-TPP in toluene solution. The morphology and structure of the composites have been investigated using Fourier Transform infrared (FTIR), X-Ray diffraction (XRD), scanning (SEM) and transmission (TEM) electron microscopy techniques which suggest formation of nanosized clusters of M-TPP around MWNTs surface. The present studies are aimed at preparing nanomaterials based devices for detection of harmful chemicals like benzene, toluene and xylene in the vapor form. The resistivity of the prepared nano-composites is found in the 10^3 to 10^4 Ω cm range. We monitored relative resistance changes of the films prepared from the nano-composites on exposure to vapors of BTX chemicals at room temperature and present the results in this communication.

Experimental

Materials

Multiwall carbon nanotubes and M-TPP were purchased from Sigma Chemical Co. and were used without further purification. Commercially available spectroscopic and AR grade chemicals were purchased from Merck Specialities, and Qualigens Fine Chemicals, Mumbai and AR grade solvents from CDH Analytical Reagents, New Delhi were employed in our experiments.

Preparation of composites and sensors

To begin with, the pristine MWNTs were functionalized by corona electrostatic discharge which resulted in the grafting of -OH groups to the end faces and defect sites on the walls of MWNTs. This is confirmed by the presence of bands around 3457 and 1637 cm^{-1} in the FTIR spectra of f-MWNTs resulting from O-H stretching and deformation modes respectively as shown in **Fig. 2**. We shall denote the -OH functionalized MWNTs as f-MWNTs. The active -OH groups on f-MWNTs facilitate H-bonding, π - π and other non-covalent interactions with M-TPP. Different compositions were prepared using variable amounts of f-MWNTs and M-TPP. In a typical procedure, 10 mg of f-MWNTs was suspended in 15 ml toluene and sonicated for 20 minutes to partially disperse bundled MWNTs. Weighed quantities of copper-TPP and cobalt-TPP were added to the

sonicated suspension of f-MWNTs and magnetically stirred for more than 25 h at 35 °C followed by ultrasonication for 15 min. The process was repeated few times to obtain composites of M-TPP with f-MWNTs. The prepared composites showed widely different resistivities depending upon the relative quantities of M-TPP and f-MWNTs. We utilized only those composites which showed resistances in the 0.2 to 5 kilo-ohm range for electrode gap of 2 mm.

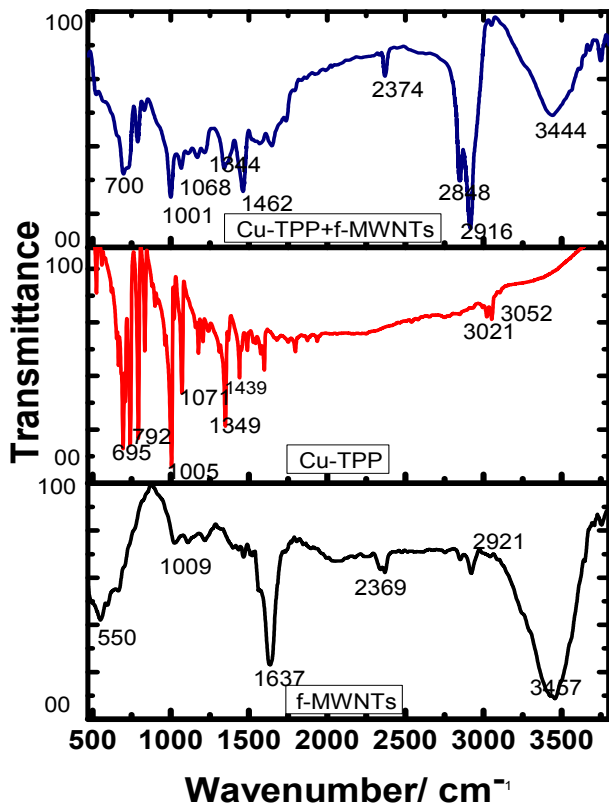


Fig. 2. Fourier-transform infrared spectra of f-MWNTs, pure Cu-TPP; and f-MWNTs + Cu-TPP composite from 500 to 4000 cm^{-1} . Some important bands showing frequency shift or intensity changes are marked.

We could not obtain good quality films of the nano-composites by spin coating technique; therefore we adopted the following approach to prepare stable films. A small drop of the nano-composite slurry in toluene on a glass plate was spread into a uniform film anchored by paraffin film. The upper surface of the film was covered by another paraffin film and sandwiched by placing a glass plate on the top of the film. The whole system was kept inside an oven at a temperature of 70 °C and heated for ~ 5 min. Sufficient care was taken to ensure that the paraffin got embedded only in the upper surface of the film of slurry which provided stability to the film. The other side of the film, not affected by the paraffin, was used to make electrical contacts using conducting silver paste for measurements. The schematic diagram of the process for fabrication is given in **Fig. 3**. Known quantities of chemicals were introduced in the glass flask of 500 ml capacity which evaporated and converted into vapors. The three way valves allowed the controlled flow of gas to be switched from dry nitrogen gas to known concentrations of BTX or other chemical vapors at almost the same pressure and flow rate.

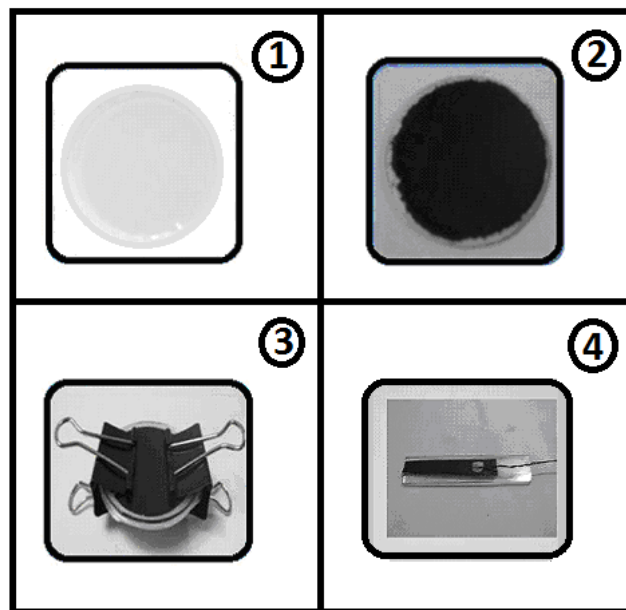


Fig. 3. Schematic diagram of the process for fabrication of sensor using paraffin film: (1) Glass plate anchored by paraffin film, (2) drop of slurry of nanocomposite in ethanol spread in the middle, (3) five paraffin films placed on the top followed by another glass plate and fastened by binder clip, kept at ~ 65 °C temperature for 5 minutes, (4) fabricated sensor from the films obtained after step 3.

These films showed good stability and could be used many times over a period of several months with high reproducibility.

Measurements

The experimental setup for measuring the change in electrical response of the sensors on exposure to BTX vapors is shown in **Fig. 4**.

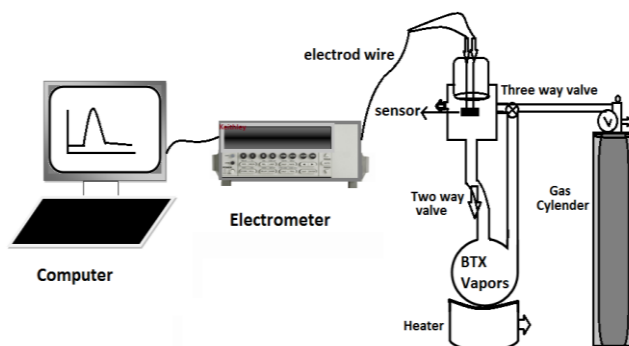


Fig. 4. Schematic diagram of experimental set-up for sensing chemical vapors using copper-, and cobalt- tetraphenylporphyrin functionalized MWNTs films.

The gas sensitive characteristics of the sensors made from the composites were investigated at ambient conditions by recording their electrical response when exposed alternately to the dry N_2 gas used as a reference and purging gas, and chemical vapors under investigation. Based on partial pressure of gases and flow rate of nitrogen gas, we estimate the concentration of benzene in the 50 ppm range for response results given in **Fig. 7** in this paper. The outlet for chemical vapors was closed after one second and the resistance of the sensor was allowed to recover its

initial value. Before starting another experiment, the chamber was flushed with nitrogen gas to remove the traces of initial chemicals. Similar experiments were conducted with other chemical vapors. The electrical current and resistance of the thin films were measured by a volt-amperometric technique using Keithley Model 6517B electrometer interfaced with a computer to store and process the data.

Experimental procedure

The samples of f-MWNTs and M-TPP prepared composites were diluted in KBr matrix to measure FTIR spectra on a Perkin-Elmer Model PE-Rx1 FTIR spectrometer having spectral resolution of 1 cm^{-1} . Transmission electron microscopy (Hitachi Model H-7650 operated at 100 kV), scanning electron microscopy (Model Hitachi S-3400N) and X-Ray diffraction (Model: Philips X'Pert Pro Multipurpose X-ray Diffractometer) techniques were utilized to get detailed information about the surface morphology and structure of the prepared composites.

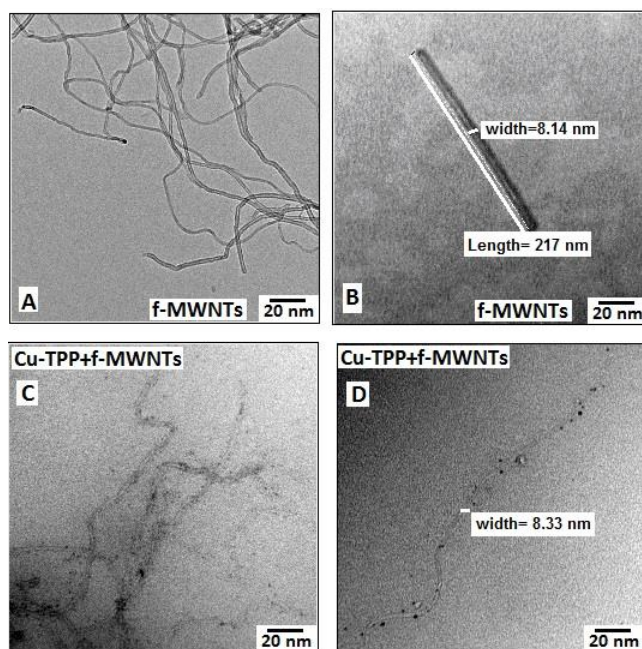


Fig. 5. Transmission electron microscopic images of f-MWNTs (A & B), and Cu-TPP functionalized f-MWNTs composite (C & D). Figs. B and D provide TEM images of an isolated f-MWNT and Cu-TPP functionalized f-MWNT for clear view.

Results and discussion

The prepared composites were characterized by FTIR, X-ray diffraction and electron microscopic techniques. The information about the morphology and structure of the prepared composites of f-MWNTs and M-TPP has been obtained by SEM and TEM microscopies. Representative TEM images of f-MWNTs displayed in **Fig. 5A** indicate three-dimensional disordered arrangement of nanotubes while **Fig. 5B** shows a single CNT with a mean outer diameter of 8.1 nm and length of 217 nm. **Fig. 5C** indicates that nanosized clusters of aggregated Cu-TPP molecules are formed around the surface of f-MWNTs while **Fig. 5D**

displays more clearly the anchoring of nanosized clusters of M-TPP around the f-MWNT surface.

The infrared spectra of f-MWNTs, f-MWNTs + Cu-TPP composite and pure Cu-TPP powder, respectively are given in the **Fig. 2** in the $500 - 4000\text{ cm}^{-1}$ spectral region. The FTIR spectra of Co-TPP based composites gave nearly similar features as of Cu-TPP based composites in the frequency range covered where mainly pyrrole related modes are expected to contribute. For comparison purposes, some bands showing frequency shift or intensity changes are marked. The broad features in the IR spectra of pure Cu-TPP are typical signatures of spectra of many M-TPP and the detailed vibrational analysis for the observed bands for Zn-TPP [24] and Ni-TPP [25] has been discussed in the past. A comparison of the IR spectra shows that bands related to the $-\text{OH}$ groups at ~ 3457 and 1637 cm^{-1} in the spectrum of f-MWNTs become weak on functionalization with Cu-TPP. There are many changes in the IR spectrum of f-MWNTs + Cu-TPP compared to spectrum of pure Cu-TPP. The IR spectrum of f-MWNTs + Cu-TPP in **Fig. 2** shows shift in the position and drastic change in relative intensity of some bands. Most of the bands broaden considerably compared to the bands in the spectrum of pure Cu-TPP powder. These changes support extensive delocalization and redistribution of π -electrons of M-TPP due to π - π electronic interactions among f-MWNTs and M-TPP. In addition, the broadening of IR bands in the spectra of nano-composites may also arise from inhomogeneous broadening due to the presence of different type of aggregates of M-TPP on the surface of f-MWNTs which give slightly different band positions resulting in overall broadening of the bands.

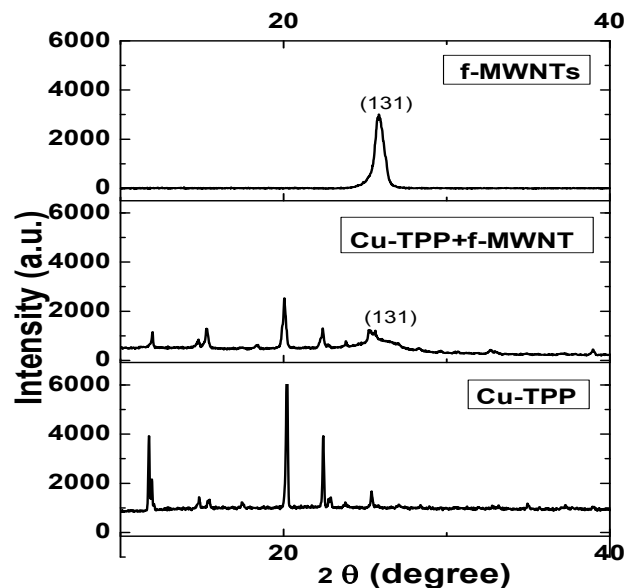


Fig. 6. X-Ray diffraction patterns of pure Cu-TPP, pure f-MWNTs; and Cu-TPP + f-MWNTs nanocomposite.

These observations along with SEM and TEM results strongly support non-covalent functionalization of MWNTs with M-TPP and formation of nanosized clusters of aggregated M-TPP molecular species around the MWNTs surface. The IR features observed in the spectra given in **Fig. 2** mainly arise from pyrrole units of the macrocycle [24,25]. The bands at 740 and 792 cm^{-1} in the IR spectrum

of Cu-TPP associated with the $\gamma_{(\text{Cb-Cb-H})}$ and $\{\gamma_{(\text{Cb-Cb-H})} + \gamma_{(\text{Cb-Cb-Ca-N})}\}$ out-of-plane modes shift to 730 and 788 cm^{-1} respectively in the spectrum of Cu-TPP + f-MWNTs nano-composite. Similarly, the IR bands at 1005, 1071 and 1349 cm^{-1} in the spectrum of Cu-TPP associated with the $\{v_{(\text{Ca-Cb})} + v_{(\text{Ca-N})}\}$ pyrrole breathing, $\{\delta_{(\text{Ca-Cb-H})} + v_{(\text{Cb-Cb})}\}$ hydrogen bending, and $\{\delta_{(\text{N-Ca-Cm})} + \delta_{(\text{Ca-N-Ca})} + v_{(\text{Ca-Cm})}\}$ pyrrole half ring modes shift to 1001, 1068 and 1344 cm^{-1} respectively in the spectra of Cu-TPP + f-MWNTs nano-composite. These results suggest weakening of the pyrrole bonds of Cu-TPP after functionalization with MWNTs.

Small shift in scattering angles of few peaks and large decrease in the intensity of the f-MWNT peak ($2\theta = 26.45$ degrees) in the X-Ray diffraction pattern given in Fig. 6 in the nano-composites compared to f-MWNTs lend support for significant electronic interaction between MWNTs and M-TPP in the nano-composite.

We have conducted different experiments to determine the response and recovery times as well as change in resistance of the composite films for detection of BTX vapors. The sensors made from composites comprising of f-MWNTs and Cu-TPP show comparatively larger change in resistance on exposure to BTX vapors compared to the sensors made from Co-TPP and f-MWNTs and the details are given in Table 1.

Table 1. Change in resistance, response and recovery times for Cu-TPP & Co-TPP functionalized MWNTs nano-composite based sensors on exposure to ~50 ppm concentration of benzene, toluene, and xylene vapors.

Type of Vapors	% change in Resistance ($\Delta R/R_0$) X 100		Response Time (sec)		Recovery Time (sec)	
	CuTPP+ f-MWNTs	CoTPP+ f-MWNTs	CuTPP+ f-MWNTs	CoTPP+ f-MWNTs	CuTPP+ f-MWNTs	CoTPP+ f-MWNTs
Benzene	4	1.7	6	4	~42 ^a	15
Toluene	6.8	1.1	5	10	~46 ^a	13
Xylene	6.3	3.1	6	10	~48 ^a	35

^aThe de-adsorption of vapors from the Cu-TPP functionalized MWNTs sensor after exposure to BTX vapors is very slow after ~30 seconds and therefore the recovery times given in the table are the best estimated values.

Figs. 7A to F show the variation of resistance and response of the two sensors based on Cu-TPP and Co-TPP functionalized f-MWNTs nano-composites on exposure to benzene, toluene and xylene vapors for a second under conditions described in the experimental section.

The response (S) of the sensor at a given concentration of vapor is defined as $S = [(R_{N_2} - R_{\text{vap}})/R_{N_2}] \times 100$, where R_{vap} and R_{N_2} are the resistances of the sensor under exposure of BTX chemical vapors and N_2 gas, respectively. The recovery time is defined as the time to reach 90% of the total resistance change. It is clear that different analytes show differential changes in the three parameters monitored in our studies, namely resistance, response and recovery times and this can be analyzed to differentiate individual component using statistical analysis techniques

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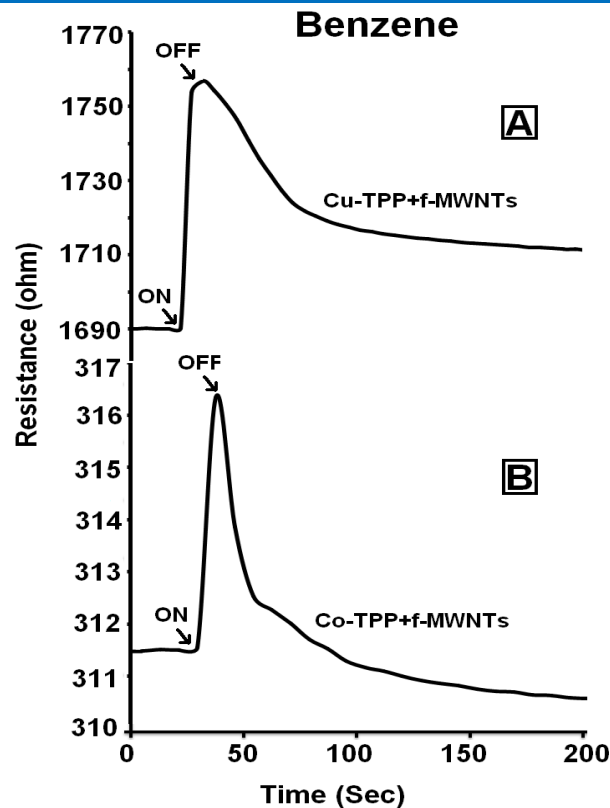


Fig. 7. (A and B) Response and variation of resistance of the sensors made from films of nanocomposite of Cu-TPP and Co-TPP functionalized f-MWNTs on exposure to ~50 ppm concentration of benzene.

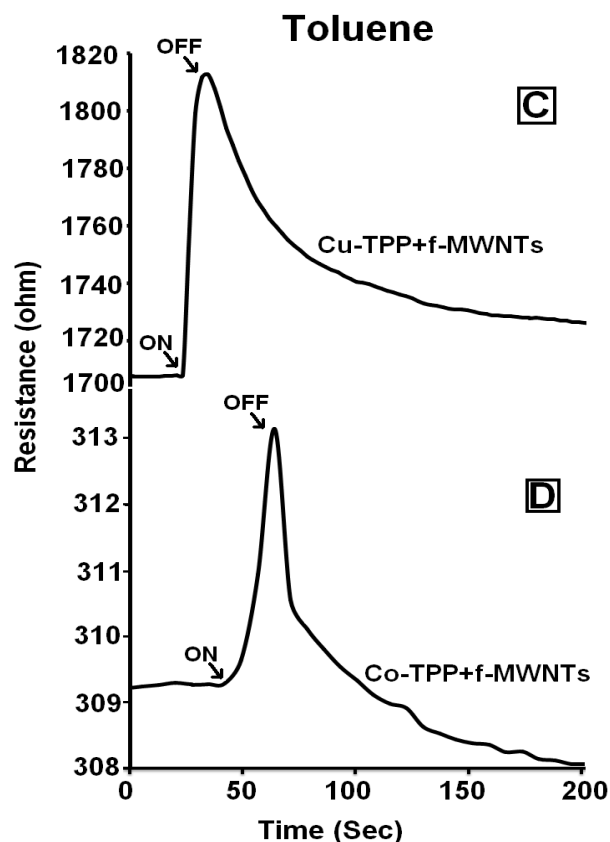


Fig. 7. (C and D). Response and variation of resistance of the sensors made from films of nanocomposite of Cu-TPP and Co-TPP functionalized f-MWNTs on exposure to ~50 ppm concentration of toluene.

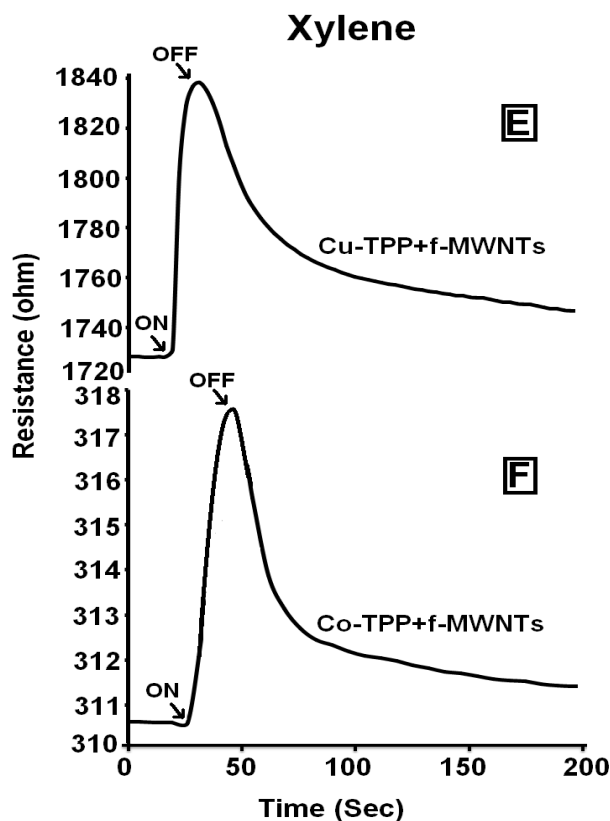


Fig. 7. (E,F). Response and variation of resistance of the sensors made from films of nanocomposite of Cu-TPP and Co-TPP functionalized f-MWNTs on exposure to ~ 50 ppm concentration of xylene

In order to check reproducibility of the data and reversibility of the sensors, we exposed the Co-TPP functionalized f-MWNTs based sensor to ~ 25, 50 and 100 ppm vapors of benzene. The response of the sensor is given in Fig. 8 and establishes that the sensing process is highly reproducible and reversible. We could get reasonable response down to ~ 5 ppm levels of BTX vapors and did not find any noticeable change in the sensing properties even after storing the sensor devices for several months.

M-TPPs are highly conjugated macrocyclic systems and known p-type semiconductors while the π -electron rich MWNTs may act as electron acceptor or donor depending upon the reacting species. The π - π electronic, H-bonding and other non-covalent interactions between f-MWNTs and M-TPP may affect the π -conjugated electronic system of the M-TPP/MWNTs composite with consequent modifications in the conductivity of the composites formed. The M-TPP molecules get attached and anchor the surface of carbon nanotubes in the form of nanosized clusters which consist of aggregated M-TPP molecules (Figs. 5C & D).

Sensing mechanism

The electrical, chemical and physical properties of MWNTs are affected by functionalization with M-TPP on formation of nano-hybrid structures. Moreover, the electronic properties of films of these nano-composites can be modulated by interaction with different chemicals. Films of pure M-TPP when exposed to oxidizing agents (electron acceptors) like NO_2 , SO_2 , halogens etc. show an increase in

electrical conductivity by generating extra charge carriers (holes), while reducing agents (electron donors) like NH_3 , CH_3OH , CO_2 etc. trap charge carriers and decrease electrical conductivity. In our sensors made from nano-composites of f-MWNTs functionalized with M-TPP, the M-TPP clusters act as receptors for BTX molecules while conductivity of the sensors is governed by MWNTs.

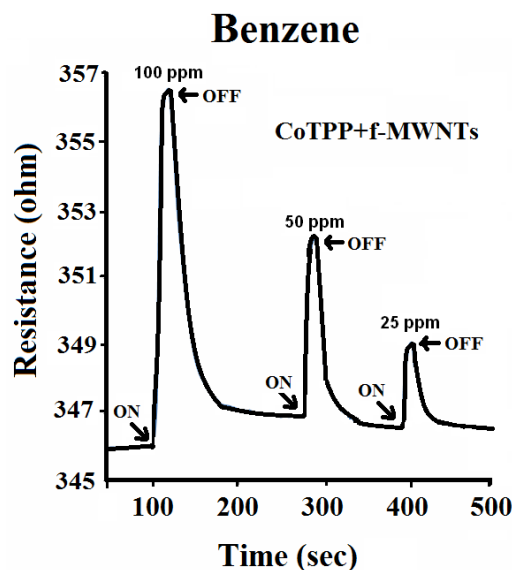


Fig. 8. Response of sensor made from films of nanocomposite of Co-TPP functionalized f-MWNTs on exposure to benzene vapors at different concentrations.

The fast response and recovery times of the sensors to BTX vapors implies that BTX molecules must interact weakly and reversibly with the M-TPP functionalized f-MWNTs composite films. The BTX molecules are initially adsorbed on the surface of M-TPP which has two possible sites for gas adsorption: one is the central metal itself and the other is the conjugated π -electronic system of the M-TPP macrocycle. At the metal site, the major interactions occur via $\pi(d_\pi)$ electrons of the metals with the electronic configuration of the analytes. The interaction at the metal site is facilitated by the chemical properties of the metal such as electronegativity and spin state [12]. Thus cobalt having higher electronegativity than copper is expected to show higher response towards BTX molecules compared to the copper based nano-composites. Contrary to this, we have observed higher response from the copper-based compared to the cobalt-based nano-composite sensors under similar conditions. This rule out interaction of analytes with the metal in M-TPP as a major contributor in sensing of BTX vapors.

We therefore expect that the BTX molecules would interact with the periphery of the macrocycle of M-TPP. In the case of conjugated and cyclic ring compounds as analytes, the main interaction route may be via the electron donating or electron accepting mechanism between the π -electrons of M-TPP and analytes. It is therefore logical to conclude that BTX molecules on adsorption on the surface of M-TPP based composite interact with the M-TPP periphery leading to partial electronic charge transfer from BTX molecules to M-TPP as per scheme given below:



In this process, electrons are donated from BTX molecules to M-TPP producing donor states below the Fermi energy level of M-TPP. Ionization of these donor states releases electrons to the valence band of M-TPP. The electrons donated to the valence band partially reduce the density of charge carriers (holes) in M-TPP. The reduced hole density of M-TPP, in turn, will affect the π -conjugated electronic system of the MWNTs and partial electronic charge transfer from M-TPP to MWNTs may lead to decrease in the conductivity of MWNTs in the M-TPP/MWNT nano-composites. The extent of charge transfer would be dependent on the type of BTX molecules (benzene, toluene or xylene) and thus may result in differential changes in the resistance, response and recovery times. In other words, changes in electronic configuration of M-TPP nanoclusters on exposure and interaction with different BTX molecules affect the electronic configuration and conductivity of f-MWNTs in the M-TPP/MWNT nano-composite differently leading to differential changes in response of the sensors for the BTX molecules. The working of these sensors can be satisfactorily explained in this frame work.

Conclusion

We have successfully prepared nano-composites by non-covalent functionalization of MWNTs with M-TPP where nano-sized clusters of M-TPP molecular aggregates anchor the MWNTs surface. The nano-composites have been utilized to fabricate sensitive sensors for detection of BTX in vapor form. The sensors show differential changes in resistance, response and recovery times on exposure to benzene, toluene or xylene vapors. Our results are very encouraging for fabrication of sensitive sensors for detection of BTX molecules at normal temperature. Further studies are in progress to explore these sensors for detection of some more volatile organic compounds for better understanding of the detailed mechanism of sensing, selectivity and limit of detection for different chemical vapors.

The sensors made from the nano-composites have many applications and advantages. The sensors can be coated on the glass, plastics or irregular shaped materials, very easy to fabricate, have very fast response and recovery times of few seconds, can be operated at room temperature under ambient conditions.

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