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Carbon Nanostructure-Based Sensors

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Dedication

To My Mother
ABSTRACT OF THE DISSERTATION

Carbon Nano Structure-Based Sensors

by

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Dr. Ashok Mulchandani, Chairperson

One-dimensional (1-D) nanostructure-based sensors provide better sensitivity as compared to conventional thin film-based sensors due to their comparable dimensions with respect to Debye length. Single-walled carbon nanotubes (SWNTs) are 1-D nanostructures having high electrical mobility, high mechanical strength and high specific surface area that facilitate building of low-power, ultrahigh density sensors within limited space. However, pristine SWNTs posses limited sensitivity and selectivity. This sensitivity issue could be resolved through surface modification of SWNTs with suitable recognition molecules. Choosing the right functional material, sensor performance, in terms of sensitivity, could be enhanced. The selectivity issue could be overcome by making an array of sensors using different functional material and combining them with suitable pattern recognition software and thus, developing an electronic nose.

The overall objective of this dissertation is the development of a high density sensor array using single-walled carbon nanotube (SWNT) hybrid structures as building blocks for the realization of highly sensitive and discriminative sensors for monitoring of
To conceive such desired sensor characteristics, SWNTs were functionalized with organic macromolecules like porphyrins and calixarene to target VOCs in the air, and with biomolecules like polyT (a ssDNA) to target mercury ions in water. Detailed analysis of SWNT hybrid formation through different routes such as solvent casting and electrochemical techniques using macromolecules was performed to investigate structure property relations and the effect of macronucleus towards sensor performance when exposed to various analytes. The SWNT-porphyrin hybrids exhibited a discriminating capability of VOCs at room temperature. However, electrochemically modified (as opposed to solvent casting) SWNT-poly(porphyrin) hybrid improved sensor sensitivity further, retaining their discriminating capabilities and providing a sub-ppm limit of detection towards VOCs. The SWNT-poly(metalloporphyrin) hybrids also showed a probable relationship between sensor response and metal present within the porphyrin depending on the metal electronegativity. ssDNA functionalized SWNT hybrid exhibited highly selective and sensitive sensing response towards mercury ions in solvent phase.
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CHAPTER 1

Introduction

1.1 Introduction:

Since the last few decades, our planet is continuously facing several serious issues and challenges. Deterioration of environmental conditions, in particular, the degradation of air and water quality is one of them. The rapid industrialization due to technological advancement throughout the globe, unscientific disposal of industrial effluents and solid waste and an exponential increase of automobile vehicles are a few of the direct causes which contribute towards the degradation of air as well as water quality. Therefore, there is a serious need for reliable, user friendly and cost effective tools to identify and quantify the pollutants that will help us take preventive measures to protect our environment.

Detection of VOCs is important for indoor and outdoor air quality monitoring. Many VOCs are used as a solvent and as a base raw material in chemical process industries. For example, ketones (e.g. acetone and methylehtyl ketone), alkanes (e.g. hexane), alcohols (e.g. ethanol) and aromatics (e.g. benzene and toluene) are widely used as a solvent, and formaldehyde is used as a base raw material in the resin industry. BTEX compounds are considered as environmental pollutant, generated by the automobile vehicles. Most of these VOCs are toxic and/or carcinogenic. Long-term exposure of these VOCs has an adversary health effect and it can also cause cancer. Hence, VOCs detection
is necessary to protect the indoor and outdoor air quality and to provide occupational health safety at the working place.

Heavy metal contamination, in particular mercury (Hg) contamination in aquatic environments is a worldwide concern due to their toxicity and biomagnification in food webs. They can accumulate in human body through consumption of contaminated vegetables and/or water, and may cause adversary health effect. An elevated exposure to mercury can affect the cardiovascular system, gastro-intestinal system, liver, kidneys and neurological system of the human body.\(^1\) Hence, detection of mercury is important for water quality monitoring and also for human health safety.

In spite of the recent advances, the task of identification and quantification of pollutants in a complex environment containing thousands of interfering species using an inexpensive, reliable device remains a difficult challenge. The most commonly used analytical methods for pollutant/contaminant detection are spectroscopy and separation-based techniques, including gas chromatography/mass spectrometry (GC/MS) and atomic absorption spectroscopy (AAS). These techniques are reliable and the tools developed based on these techniques are very sensitive. However, they are slow and expensive. They also need trained manpower to be operated and are not easy to be deployed in the field due to their bulky size. Portable GC devices have also been developed using various detectors, but they still have disadvantages such as limited sensitivity and selectivity, increased cost and size incompatibility for many applications.\(^2,3\) Moreover, separation based tools are not applicable in continuous monitoring applications. Because of these
limitations in conventional analytical tools, chemical sensors have emerged as an alternative to meet the current requirements.

A Chemical sensor is a device that can detect and/or quantify the presence of analytes by transforming chemical information generated through the analyte-sensory element interaction into an analytically useful signal. Chemical sensors can be categorized depending on their detection principle, construct and application. A series of different detection principles, such as a change in electrical properties (e.g. conductivity), optical properties (e.g. absorption, fluoresce, color etc.), electrochemical activity, dielectric properties and magnetic properties are currently utilized for the development of chemical sensors. Among them, sensors based on the change in electrical property remain an attractive option due to their simple operation, facile fabrication process and device configuration. They typically operate by measuring the change in conductivity of the sensor upon adsorption of the analyte molecule on the sensory element.

The most important requirements of a good sensor are high sensitivity and selectivity towards the target analyte along with a number of other requirements such as high reliability, low response and recovery time, low cost, energy efficiency, easy scalability and easy operability.

Sensitivity of sensors can be improved by reducing the dimensions of the sensing material. When these dimensions are reduced to the nanometer range, the sensors exhibit size dependent electrical and optical properties and deviate substantially from their bulk properties. These nanomaterials also provide a large surface-to-volume ratio, which
causes the surface phenomena to dominate over the chemistry and physics that are observed in the bulk. This results in a significant material property change and thus sensor sensitivity improves. The advancement in the field of nanotechnology facilitates the synthesis of wide range of nanomaterials which are used to build highly sensitive sensors using nanostructure material. Further, with the recent developments in the field of lithography, low power microelectronics and pattern recognition algorithms facilitate the miniaturization process of the sensor dimension and allow us to integrate large numbers of sensor devices within a small area to make an electronic nose – a device capable of detecting multiple analytes from within a complex mixture by comparing the unique figure prints or response patterns of the components.

The main focus of this thesis is the development and demonstration of nanosensors for detection of volatile organic compounds (VOCs) in air and mercury in aquatic environment.

1.2 Nanomaterials Based Sensors:

Materials, which have a dimension less than 100 nm, are known as nanomaterials. Nanotubes, nanorods, nanowires and nanobelts are a few examples of nanomaterials and they are generally called one-dimensional nanomaterials.

In a chemiresistive sensor which works based on the principle of the materials conductivity change, when a charged/ionic analyte molecule binds to the surface of the sensor, a zone of charge accumulation/depletion is formed on the sensor surface depending on the injection/withdrawal of the charge carrier to/from the sensor element
causing a change in resistance/conductance of the sensing material. The use of one-dimensional nanostructures for the development of chemiresistive sensors has a definite advantage over thin-film based sensors. In a thin-film based sensor, the zone of charge accumulation/depletion is only a fraction of the total cross-sectional area. As a result, the current can easily bypass the affected zone and that, in turn, leads to suppression of the sensing signal. However, in the case of one-dimensional nanostructure-based sensors, the entire cross-section is induced by the affected zone because of their comparable diameter with the depth of the affected zone (figure 1). Hence, the current cannot bypass the affected zone resulting in an electrical conductance/resistance change and thus making these sensors more sensitive than the thin film sensors. Furthermore, one-dimensional nanostructures can easily be configured as field-effect transistors (FETs) using lithography techniques and can be potentially integrated with the modern microelectronics.

1.2.1 Metal Nanostructure Based Sensors:

Metallic nanowires are highly electrically conducting and chemically stable materials. These properties of metal nanowires make them useful in the field of electrical circuit integration. Upon surface absorption of the analyte molecules, the electrical properties of these nanowires change mainly due to boundary layer electron scattering and “chemical gating” effects, thereby making them an attractive material for sensor applications. The metal nanowires can be synthesized using both template-less and template-directed electrochemical, chemical and mechanical methods. However,
The template directed electrochemical methods like lithographically patterned nanowire electrodeposition (LPNE) provide in-situ growth and direct integration of the nanowires in the sensor device.\textsuperscript{7,14} The electrochemical method provides precise control over the fabrication process and morphology, and the lithographic processes provide an option of manipulating the dimensions of the nanowires. Various groups have successfully demonstrated the detection of gaseous analytes like H\textsubscript{2}\textsuperscript{14-18}, NH\textsubscript{3}\textsuperscript{11} and amine vapors\textsuperscript{11} using metals nanowires like Pd\textsuperscript{15-17} and Ag\textsuperscript{11}.

The major advantages of the metal nanowire based sensors are (1) room temperature operation, (2) faster response and (3) low power consumption. However, their high charge carrier capacity with respect to the semiconductors makes them almost inert to several analytes, in particular to the weak binding molecules like VOCs that limits their possible exploration in the future.

1.2.2 Metal Oxide Nanostructure Based Sensors:

Chemical and physical properties of metal oxide semiconductors such as In\textsubscript{2}O\textsubscript{3}, ZnO, and SnO\textsubscript{2} have been extensively studied for the last few decades. Metal oxide thin film based solid-state chemical sensors have been developed and successfully commercialized by exploiting their material properties change caused by the surface adsorption process. The detection principle mainly relies on the conductance change of the material based on the interaction between the analytes and the oxygen vacancy sites available on the oxide surface. The oxygen vacancies, created due to the molecular adsorption on the oxide surfaces, are chemically and electrically active. When vacancies
are created they tend to bind with more atoms or molecules and the electrons that are left behind form a space charge region (SCR) closer to the oxide surface.\textsuperscript{19-21} As a result, when charged molecules bind to the surface, they either donate or accept electrons to or from the SCR depending on their charge types and change the conductivity of the oxides.

The limited sensitivity is one of the major drawbacks for the available commercial sensors. This can be overcome by using one-dimensional nanostructures because of their comparable diameters with respect to the width of the SCR.

Several physical and chemical methods have been developed for synthesizing one-dimensional oxide nanostructures. Solution phase growth,\textsuperscript{22} chemical vapor deposition (CVD),\textsuperscript{23, 24} laser ablation,\textsuperscript{25} electrochemical methods followed by annealing\textsuperscript{19, 20} have been demonstrated to produce single-crystal and polycrystalline oxide nanowires,\textsuperscript{19, 25, 26} nanotubes,\textsuperscript{20, 23} and nanobelts\textsuperscript{27}. Using these nanostructures, sensitive detection of various analytes such as NO\textsubscript{2},\textsuperscript{26} NH\textsubscript{3},\textsuperscript{26} and H\textsubscript{2}\textsuperscript{29} have been demonstrated. Further, sensitivity enhancements by doping the nanostructures and functionalizing with catalytic metals have also been reported.\textsuperscript{22, 29}

Despite sensitivity and stability of metal oxide nanostructure chemiresistors and Chem-FET\textsuperscript{19} demonstrate them to be excellent candidates for the next generation of miniature gas sensors, high operational temperature requirement and the inertness towards VOCs limit their application within a specific domain.
1.2.3 Conducting Polymer Nanostructure Based Sensors:

Conducting polymers (CPs) such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTH) and poly (3,4-ethylenedioxythiophene) (PEDOT) are attractive classes of organic materials, which exhibit unique electronic properties while retaining mechanical flexibility and ease of processing. CPs are organic polymers which can be “doped” or “dedoped” through chemical and electrochemical processes. Their conductivities can also be altered from a near metallic (1 S/cm) to an insulating ($10^{-10}$ S/cm) regime by varying the dopant type and concentration. The prominent features of CPs such as tunable charge transport properties, stability at ambient conditions along with the property of being chemically active at room temperature make them ideal for the use as a transducing material in chemical sensors.

Over the past few years, CPs based thin and thick film sensors have been demonstrated for the detection of a wide variety of analytes ranging from biomolecules to gaseous pollutants. However, in recent times, focus has been shifted to the use of one-dimensional CPs nanostructures as a sensory element due to the advantages mentioned earlier.

Kaner and coworkers synthesized PANI nanofibers through chemical polymerization, fabricated PANI nanofiber network-based sensor and demonstrated the sensor performance enhancement over the conventional PANI thin film sensors. The higher surface area, porosity and nanometer range diameter of the PANI nanofibers contributed towards the sensor signal enhancement.
Liu et al. has demonstrated single PANI nanowire based chemical sensor, fabricated by using a nanolithographic deposition process, which showed a rapid and reversible resistance change upon exposure to NH$_3$ at concentrations as low as 0.5 ppm.$^{33}$

Hangarter et al. has reported template-directed synthesis of PPy nanowires, their integration on a prefabricated microelectrode by drop casting/electrophoretic alignment and successful demonstration towards NH$_3$ detection.$^{38}$

Yaping et al. have also used the template-directed method to fabricate their Au-PEDOT/PSS-Au nanowires, assembled on a prefabricated gold electrode by dielectrophoretic alignment method and demonstrated the effectiveness as a sensor towards VOCs (methanol, ethanol and acetone).$^{39}$ They found a drop in resistance while the sensor was exposed to the analyte vapors, which attributed towards the swelling of the polymer resulting an increase in hopping distance. Recently Cao et al. has reported the performance enhancement of the sensors towards methanol by replacing the PEDOT/PSS nanowire with PEDOT/ClO$_4$ nanowires.$^{40}$ The possible reason for this performance enhancement of the PEDOT/ClO$_4$ nanowire sensor is due to domination of the partial charge transfer between the polymer and the absorbed analyte as opposed to the increase in hopping distance due to swelling of polymer.

Although CP nanostructures based gas sensors showed an excellent sensing performance in terms of sensitivity and quick response at room temperature operation, the long-term stability of the polymers for practical applications and the scalability issues due to complex fabrication process still remain a challenge.
1.2.4 Single-walled Carbon Nanotube Based Sensors:

Single-walled carbon nanotubes (SWNTs) are sp² bonded carbon based materials consisting of a single graphene sheet seamlessly wrapped up into a cylindrical tube. SWNTs are one-dimensional nanostructures that are approximately 0.4 to 3 nm in diameter and few hundred microns long. The structure of SWNTs provides them with inherently unique electrical, physical and chemical properties. Mechanically, SWNTs are the strongest fibers among the known materials due to the C-C bond. Thermally, they have high thermal stability in both vacuum and air. Electronically, they can be either metallic or semiconducting in nature depending on their diameter and the helicity of the arrangement of graphitic ring in their wall. SWNTs' nanometer range diameter and high electrical transport property make them potential candidates for many microelectronic applications. Their superior electrical conductivity as compared to other semiconducting materials facilitates the development of low-power electronic devices and their smaller size facilitates the miniaturization process to build high-density nanosensor arrays within smaller areas.

All carbon atoms in SWNTs are surface atoms and they are exposed to the environment. These exposed carbon atoms facilitate the surface adsorption process. When SWNTs are exposed in a gaseous atmosphere, the gas molecule adsorption causes the charge transfer between the molecules and the nanotubes, resulting in a measurable electronic property change, in particular, the conductivity change of the nanotubes. Furthermore, the thermal stability of the SWNTs along with their remarkable electronic
property change due to surface absorption when exposed to gaseous analytes make them perfect material for solid-state chemical nanosensors. Kong et al.\textsuperscript{49} and Collins et al.\textsuperscript{50} showed good sensitivity towards the detection of active gas molecules like NH$_3$, NO$_2$ and O$_2$, and Kim et al.\textsuperscript{51} demonstrated Hg ion detection using semiconducting SWNTs and established them as a promising sensing material. However, the range of molecules that can be detected by the SWNT-based sensors is limited depending on their binding energies and thereby the charge transfers with the SWNTs. Gas molecules such as carbon monoxide and most of the VOCs can hardly be detected due to the low binding energy with the SWNTs or almost negligible adsorption on the SWNTs surface.\textsuperscript{46} However, this limitation could be overcome in two possible ways, (1) by modifying the electronic and chemical properties of the SWNTs through substitutional doping\textsuperscript{52} of impurity atoms (boron and nitrogen) into intrinsic SWNTs or (2) by surface modification of SWNTs with a suitable recognition molecule that has greater affinity towards the target molecule.\textsuperscript{53, 54} Surface functionalization/modification of SWNTs can be done using covalent and non-covalent binding approach. Significant improvements in sensing performance were observed for NH$_3$ detection when SWNTs were functionalized covalently with poly (m-amino benzene sulfonic acid) (PABS).\textsuperscript{54} Sensitivity enhancements were also observed for H$_2$ detection when SWNTs were functionalized noncovalently with palladium nanoparticles that catalyzed the surface adsorption process.\textsuperscript{55} Electrochemical functionalization processes with metal and metal oxide nanoparticle and conducting polymer have also been reported for sensitivity enhancement towards analyte detection.\textsuperscript{53, 56} All of these demonstrations were based on chemiresistive mode of sensor configuration.
where the changes in sensor resistance were recorded as a function of gaseous analyte concentration. When two metal contacts are connected to each end of an individual semiconducting SWNT, the metal/SWNT/metal device exhibits p-type transistor characteristics. Therefore, the resistance response of SWNTs to gas adsorption can be detected with field effect transistors (FETs). Kong et al. reported an SWNT-FET transistor for chemical sensing. Lurdes et al. and Someya et al. demonstrated the detection of BTEX (benzene, toluene, ethylbenzene and Xylenes) by using the same FET configuration.

1.3 Porphyrin Based Sensors:

Porphyrins (figure 2) are organic macrocyclic chemically stable compounds having interesting structural, chemical and optical properties. They are composed of four modified pyrrole subunits linked together by four methine bridges. These compounds are large delocalized π aromatic systems having flat and planar structures. The presence of four nitrogen atoms in the center of the macrocycle makes them the most versatile chelating system and hence they can coordinate with almost all the metals and non-metals present in the periodic table. When the coordinated metal atom present within the porphyrin ring structure is in an unsaturated state, it can bind with one or two additional ligands at the axial position. For example, in the living systems, iron protoporphyrin IX can bind with dioxygen in a reversible way through a fine control of the coordination axial site, mediated by the protein pocket. The change in the peripheral subunits of the porphyrin may also influence the electronic distribution in the π aromatic
system of the macrocycle, resulting in influencing the interaction between the porphyrin/metalloporphyrin and the analyte molecules. For example, an electron withdrawing subunit in a metalloporphyrin system will augment the positive charge on the coordinated metal leading to a stronger interaction with the electron donating analytes. Apart from the metal coordination interaction, other weaker interactions, such as the van der Waals forces or hydrogen bonding may also take place between the porphyrin and the analyte molecules. Any of these interactions, alone or in combination, can change the physicochemical properties of the porphyrin significantly. These properties change through various porphyrin-analyte interactions and the abundance of a wide range of synthetic porphyrins having different peripheral subunits and central metal atoms makes the porphyrins a potential building block for the development of chemical sensors or sensor arrays.

The sensitivity of the porphyrin based chemical sensors towards the target analyte could be enhanced by choosing the right porphyrin. The choice of the porphyrin can be made judiciously by understanding the chemistry involved between the porphyrin and the analyte. An empirical rule based on Hard-Soft Acid-Base (HSAB) principle, which states that hard acid (metals) prefers to bind with hard bases (analytes) and vice versa, could be helpful for choosing the right porphyrin for the target analyte. For example, nitrogenous compounds like amines could more efficiently bind with the rhodium (Rh) coordinated porphyrin than manganese (Mn) coordinated porphyrin as Rh is more of a hard acid than Mn. Recently, a theoretical work with pthalocyanines, which is analogous to porphyrin, confirmed the effectiveness of the above-mentioned rule by using density functional
theory (DFT).⁶¹

Porphyrians have an affinity towards most of the organic compounds. Hence, tremendous efforts have been put forward since last the two decades for the development of porphyrin based sensors for VOCs detection. Suslick and coworkers have exploited the photophysical properties of porphyrins and demonstrated the effectiveness of porphyrin as an optical transducer based on color change for the detection of a wide range of VOCs like alcohols, ketones, aldehydes, organic amines and organic acids after printing the porphyrin on an inert porous substrate like silica gel plate, acid-free paper, nylon or poly(vinylidene fluoride)⁶². However, these sensors cannot perform up to their full potential in humid atmosphere. Afterwards, the authors have shown that they can overcome the humidity issue by encapsulating the porphyrines in a hydrophobic organosol matrix.⁶³-⁶⁶ These sensors can discriminate the VOCs one from the others and can detect the analytes at concentrations as low as a few ppb. But, these sensors can be used only for one time and cannot be used for continuous real time purposes.

Natale and coworkers have successfully modified the quartz crystal microbalance (QCM) probe with various porphyrins by simple solvent casting techniques and demonstrated their utility as sensors for food quality monitoring purposes by detecting VOCs with the help of suitable pattern recognition algorithm.⁶⁷, ⁶⁸ Solvent casting technique generally provides a non-uniform coating and therefore the performance of the QCM may be compromised. Anticipating this problem, they replaced the solvent casting technique with Langmuir-Blodgett (LB)⁶⁹ and electropolymerization⁷⁰ technique that
could provide a uniform thickness and demonstrated the improvement in sensor sensitivity.

For many practical applications, the effective utilization of the above mentioned porphyrin-based chemical sensors are limited by their complex architecture, large volumes (poor portability) and/or limited sensitivity.

Porphyrrins are semiconducting in nature and hence can be used as a transducer in a solid-state sensor.\textsuperscript{71} An interesting and facile way of porphyrin-based nanotube synthesis, relying on ionic self-assembly of two opposite ionic charges, has been reported by Shelnutt and coworkers, where the nanotube is of 50-70 nm in diameter and few hundreds of nanometers in length.\textsuperscript{72, 73} But the integration of those nanostructures for the realization of a solid-state sensor still remains a great challenge due to their stability and incompatibility with the lithographic processes. Further, porphyrin’s limited conductivity is the hardest impediment towards the development of solid-state sensors exclusively based on porphyrins.\textsuperscript{74} Recent attempts have been made to develop porphyrin based thin-film conductometric sensors using a discontinuous gold film as a support material\textsuperscript{75} and a sol-gel matrix containing SnO\textsubscript{2}\textsuperscript{76} to overcome the conductivity issue. However, these devices showed poor performance in terms of sensitivity.

Porphyrrins have very recently been used as functional materials to improve the sensitivity of sensors by exploiting their affinity towards VOCs. Silicon semiconductor\textsuperscript{77} and multiwalled carbon nanotubes\textsuperscript{60} have been successfully modified with porphyrins and demonstrated their superior sensing capability towards organic amines and other VOCs.
1.4 Calixarene Based Sensors:

The calix[n]arenes (figure 3) are a group of oligophenolic, macro-cyclic compounds linked by methylene bridges (figure 1).\textsuperscript{78} They are formed by hydroxyalkylation processes of a phenolic compound with an aldehyde. The most accessible calix[n]arenes are tetramers, hexamers and octamers, (\(n = 4,6\) and 8 respectively). They possess a bowl like structure, having an upper rim defined by para-substituents of the phenolic rings, and a lower rim defined by the phenolic hydroxyl groups. A hydrophobic cavity lies in between these two rims whose boundaries are the inside \(\pi\)-surfaces of the constituent aromatic rings. By appropriate substitution at the hydroxyl groups and by attaching additional substituents to the para positions, their structures can be easily customized as per requirements.

Calixarenes possess interesting optical and tunable chemical properties as well as good chemical stability.\textsuperscript{79, 80} Their ability to interact with the analyte molecules through weak van der Waals forces, the change in measurable properties upon calixarene-analyte binding and structural conformational change depending on the analyte makes them an attractive class of sensing materials.\textsuperscript{81} By choosing the right calixarenes depending on the size compatibility of the analyte molecule with their cavity size and their end-terminal functional groups, sensitive and selective sensors can be developed. Moreover, the commercial availability of a wide variety of calixarenes having different functional groups and cavity sizes and the flexibility in their synthesis provides us with an option to develop sensor arrays based exclusively on calixanenes.
For the detection of enantiomers of amine\textsuperscript{80} and nitrogen dioxide\textsuperscript{82} in the solution phase, colorimetric detection principle has been demonstrated through visual observation by exploiting the structure switching capability of the calixarenes and by capturing the analyte molecule within the calixarene cavity, respectively. Calix also forms a highly porous structure when prepared as a thin film. Their porous structure and binding ability towards analytes facilitate the surface adsorption process causing a change in mass and refractive index of the film. A small change in mass can modulate the sensor signal in a QCM device.\textsuperscript{83} On the other hand, the change in refractive index can modulate the sensor signal by modifying the surface plasmon resonance angle in a SPR device.\textsuperscript{84-86} Several groups have reported real-time VOCs and gas sensing using QCM and SPR platforms. The change in surface morphology due to swelling of the calixarene film is mainly responsible for the change in refractive index.

Different groups have reported calixarene based nanotube syntheses. However, they are a few nanometers in length.\textsuperscript{87, 88} Incorporation of those ultra small nanostructures on a substrate is a huge challenge and impossible with the available tools and techniques. Hence, fabrication of a solid-state chemical nanosensor based on calixarene is still far from the reality. Poor electrical conductivity of the calixarenes is another impediment towards the use of calixarenes as a transducer in a solid-state chemical sensor.\textsuperscript{89} However, several groups have used calixarenes as functional materials exploiting their binding ability with the analytes to improve the sensing performance of chemical sensors.\textsuperscript{90}
1.5 Objectives of the Thesis:

In light of the above discussion, by understanding the importance of one-dimensional nanostructure and the potential of SWNT based hybrid structures for wide range of analyte detection the overall objective of this thesis is fixed on three specific aims.

-To design and fabricate low cost and highly sensitive SWNT based hybrid sensors/sensor arrays for VOCs.

Among the nanostructures, SWNTs possess the ability to fabricate low power versatile solid-state sensor for room temperature applications. However using a simple technique such as solvent casting or a versatile technique such as electrochemistry enables efficient way of hybrid fabrication with organic macromolecules such as porphyrins and calixarenes that lead to the development of a superior sensor for VOCs. Similarly, choosing suitable biomolecules as functional materials likes polyT (a single stranded DNA) and making a SWNT hybrid, sensitive detection of mercury could be achieved. Further, one needs to consider innovative engineering strategies for the integration of large number of transducers within a compact area and individual functionalization with various functional materials for the purpose of making a sensor arrays. Thus the objective of the research work is to develop a novel cost effective, simple technique for SWNT hybrid fabrication for sensitive and discriminative detection of VOCs in atmosphere and mercury in aquatic environment.

-Structural, spectroscopic and electrical characterization of these devices to
understand the functionalization process prior to their application in sensing.

Characterization studies were performed in terms of I-V, FET, Raman and FTIR spectroscopy, C-V, SEM and AFM on the hybrid devices fabricated by the method of solvent casting/electropolymerization to obtain a clear understanding of the structural and electrical properties of the devices and to understand the functionalization processes.

- Application of the SWNT based hybrid devices in the fields of gas sensing.

To understand the sensing behavior of the sensor, sensing experiments were done at various concentrations of the test analyte in a systematic manner. The sensing performance was optimized by varying several parameters that affect the physical and electronic properties of the device. The discriminative characteristics of the sensors were also evaluated by using principle component analysis.

1.6 Organization of the Thesis:

Chapter 2 discusses the synthesis, fabrication, and characterizations of the porphyrins functionalized SWNT hybrid sensor arrays and their application in the field of sensing VOCs of interest.

Chapter 3 describes the importance of surface functionalization with the porphyrin polymers for sensitivity enhancement of the sensor. The synthesis, fabrication, and characterizations of the SWNT-poly(porphyrin) hybrid sensor and their performance evaluation towards acetone and BTEX compounds were also discussed in this chapter.
Chapter 4 illustrates the discriminative capability of the SWNT-poly(metallo-porphyrins) sensor arrays for detecting BTEX compounds and the role of different metals at the metal center of the porphyrin towards the sensing performance.

Chapter 5 deals with the synthesis, fabrication, and characterizations of the SWNT-calixarene hybrid sensor and their sensing properties towards BTEX compounds.

Chapter 6 describes the synthesis, fabrication and characterization of polyT functionalized SWNT hybrid sensors for the detection of mercury.

Chapter 7 summarizes the work done and conclusion.
1.7 References:


Figure 1.1 Schematic showing the advantage of 1-D nanostructure versus 2-D thin/thick film structure. Arrows represent the charge carrier and density. Yellow sphere denote the analyte and cone shapes correspond to the depletion zone.
Figure 1.2 The structure of porphyrins/metallo-porphyrins. The basic porphyrin unit does not have any metal atom at the center (M) and their peripheral subunits (R₁ & R₂) are hydrogen. Metalloporphyrins have a metal atom at the center, but meso-porphyrin does not have any metal. However, in both cases, lateral subunits at R₁ and R₂ position could be hydrogen or any other functional groups.
Figure 1.3 The structure of calixarenes [R = H, alkyl ; n = 4-8].
CHAPTER 2

Porphyрин-Functionalized Single-Walled Carbon Nanotubes
Chemiresistive Sensor Arrays for VOCs

Abstract

Single-walled carbon nanotubes (SWNTs) have been used extensively for sensor fabrication due to their high surface-to-volume ratio, nanosized structure, and interesting electronic property. Lack of selectivity is a major limitation for SWNT-based sensors. However, surface modification of SWNTs with a suitable molecular recognition system can enhance the sensitivity. On the other hand, porphyrins have been widely investigated as functional materials for chemical sensor fabrication due to their several unique and interesting physicochemical properties. Structural differences between free-base and metal-substituted porphyrins make them suitable for improving the selectivity of sensors. However, their poor conductivity is an impediment in the fabrication of prophyrin-based chemiresistor sensors. The present attempt is to resolve these issues by combining free-base and metallo-porphyrins with SWNTs to fabricate SWNT-porphyrin hybrid chemiresistor sensor arrays for monitoring volatile organic components in the air. Differences in sensing performance were noticed for porphyrins with different
functional groups and with different central metal atoms. The mechanistic study for acetone sensing was done using field-effect transistor measurements and revealed that the sensing mechanism of the ruthenium octaethyl porphyrin hybrid device was governed by electrostatic gating effect, whereas the iron tetraphenyl porphyrin hybrid device was governed by electrostatic gating and Schottky barrier modulation in combination. Further, the recorded electronic responses for all hybrid sensors were analyzed using a pattern-recognition analysis tool. The pattern-recognition analysis confirmed a definite pattern in response for different hybrid materials and could efficiently differentiate analytes from one another. This discriminating capability of the hybrid nanosensor devices opens up the possibilities for further development of highly dense nanosensor arrays with suitable porphyrins for E-nose applications.
2.1 Introduction:

Single-walled carbon nanotubes (SWNTs) have gained attention in sensing applications owing to their unique electrical and structural properties.\textsuperscript{1, 2} In particular, the property of conductance change in SWNTs on absorption of an analyte gas molecule makes them a potential material for sensor development.\textsuperscript{3, 4} Also, their high electrical mobility enables the development of low-power microelectronics. Further, SWNTs, one-dimensional structures with a nanometer range diameter, make it possible to develop a high-density nanosensor array within a limited space. However, the lack of sensor performance in terms of sensitivity and selectivity is intrinsic in carbon chemistry and it limits the use of SWNTs as an individual sensor.\textsuperscript{5} However, surface modification of SWNTs with a suitable guest molecule can enhance sensing performance.\textsuperscript{6-8}

On the other hand, porphyrins are organic macrocyclic compounds having interesting structural and optical properties, and chemical stability.\textsuperscript{9} They are able to bind nonspecifically with different analytes through van der Waal forces, hydrogen bonding, and coordination interactions with the central metal ion.\textsuperscript{10, 11} Further, changes in certain physical properties upon porphyrin-analyte binding makes porphyrins an attractive class of sensing material. The sensing capabilities of porphyrin thin film have been demonstrated based on optical or mass detection.\textsuperscript{12-16} Porphyrin thin-film-based field-effect transistor (FET) also has been reported as gas sensors.\textsuperscript{15, 17} Although the transduction mechanisms of the above-mentioned device are simple, fabrication may require use of complex technology. In this regard, a chemiresistive sensor based on
conductivity change could be the simplest possible transduction mechanism, which requires simple technology for electronic application. The very low electrical conductivity of the porphyrin structure makes it difficult to develop only porphyrin-based chemiresistive sensors. However, the SWNT-porphyrin hybrid, which can be prepared by surface modification of SWNTs with porphyrin, could overcome the conductivity issue. In the SWNT-porphyrin hybrid, the high electrical mobility of SWNTs improves the device conductance, whereas the binding ability of porphyrin toward different analytes improves sensing performance of the hybrid device when used as a sensory layer.

Porphyrin has a flat and planar structure that facilitates $\pi$-$\pi$ interaction and binds to the SWNTs’ surface almost without altering SWNTs’ electronic properties. Further, porphyrin can be easily tailor-made at the synthetic level by adding different functional groups at the outer porphyrin ring and by introducing different metal atoms at the core of the porphyrin ring, which could provide different transduction mechanisms depending upon the type of interaction between the porphyrin and the analyte. The richness of porphyrin library facilitates the independent development of SWNT-porphyrin hybrid based sensors arrays. There are reports on a multiwalled carbon nanotube (MWCNT)-based porphyrin hybrid sensor for sensing volatile organic compounds (VOCs). However, it requires complex sensor fabrication techniques. Also it does not explain the possible sensing mechanism.

In this work, we report a nanosensor array based on porphyrin-
functionalized SWNT hybrids operating in chemiresistive mode for a wide spectrum of VOCs. Various porphyrins, viz. octaethyl porphyrin (OEP), ruthenium OEP (RuOEP), iron OEP (FeOEP), manganese OEP (MnOEP), tetraphenyl porphyrin (TPP), ruthenium TPP (RuTPP) and iron TPP (FeTPP), were used for surface modification of SWNTs. A systematic study was done to evaluate sensing performance of the hybrid devices towards a number of VOCs. Field-effect transistor (FET) analysis was done to understand the sensing mechanism of the hybrid device. Principle component analysis (PCA) was done using sensing data of hybrid devices to determine the discrimination capability of the devices towards different VOCs. PCA results revealed clear segregation of sensing response to each gas, thus providing a unique signature of responses of different devices towards various VOCs.

2.2 Experimental Details:

2.2.1 Nanosensor Fabrication:

The SWNT solution was prepared dispersing 0.2 mg of carboxylated SWNTs [P3 SWNT-COOH, 80 ~ 90% purity from Carbon Solution Inc. (Riverside, CA, USA)] in 10 ml of N,N-dimethylformamide (DMF) (Sigma Aldrich, Spectral grade) by ultrasonication for 90 minutes, followed by centrifugation at 31,000 g for another 90 minutes to separate soluble fraction from the aggregates.

Sensor arrays were microfabricated on a highly doped p-type silicon substrate
by standard lithographic patterning. First, an approximately 100 nm SiO$_2$ insulated layer was deposited on the substrate by low-pressure chemical vapor deposition (LPCVD). Electrodes were written on the substrate by photolithography, followed by the deposition of a 20 nm Cr layer and a 180 nm of Au layer by e-beam evaporation. The width of the electrode was 200 nm and was separated by a gap of 3 µm. Finally electrodes were defined by using a standard lift-off technique.

To bridge the gap between the gold electrodes, SWNTs were aligned dielectrophoretically across the electrodes by putting 0.1 µl of an SWNT-suspended solution on the top of the electrode gap while applying 3 V$_{p-p}$ at a frequency of 4 MHz by a function generator (Wavetek, San Diego, CA, USA). Desirable resistance of the device could be achieved by varying the alignment time. After alignment, the device was washed with nanopure water to remove the extra SWNTs solution and dried by gently blowing dry nitrogen gas. The electrode was then annealed at 300°C for 90 minutes under a reducing environment (5% H$_2$ in N$_2$) to improve the contact between the gold electrode and SWNTs by removing any DMF residues between the electrode and SWNTs.

SWNTs were functionalized with different free-base and metal substituted porphyrin by the solvent casting technique. A 0.1 mM porphyrin solution was prepared in DMF for each porphyrin.

2.2.2 Gas Sensing Studies:
For gas sensing studies, the sensors were wire-bonded (West Bond Inc., Anaheim, CA, USA) to a chip holder, and each sensor was connected in series with a potentiometer. The value of the potentiometer was adjusted to a near possible value of the initial resistance of the sensor to optimize the resolution obtained from the measurement. A bias potential of 1 V was applied across the sensor to study the sensing performance. The sensor was covered with a 1.3 cm³ sealed glass dome of with gas inlet and outlet. Dry air (purity: 99.998%, Air gas Inc., Riverside, CA, USA) was used as the carrier gas. Saturated VOCs vapor was generated by passing dry air though a bubbler filled with liquid VOCs. Different concentrations of VOCs vapor were obtained by mixing the VOC vapor stream and dry air. Two mass flow controllers (Alicate Scientific Inc, Tucson, AZ, USA) were used to control the gas flow rate. A Labview program was developed in-house and used to control and monitor the voltage of the circuit using FieldPoint analog input and output modules (National Instruments, Austin, TX, USA). In all the experiments, sensors were first exposed to dry air to achieve the baseline, then to a desired concentration of analyte vapor concentration, and then back to air, which completed one cycle. A schematic diagram of the sensing system was shown in figure 2.1.

2.2.3 Characterization:

The structural characterization of SWNTs-porphyrin hybrid device was done by using a scanning electron microscope (XL-30 FEG, FEI, Oregon, USA) and an atomic force microscope (Veeco Innova, Santa Barbara, CA, USA).
Electrical characterization was done through current-voltage ($I_{DS}-V_{DS}$) measurements and field-effect transistor (FET) measurements, to confirm surface functionalization of SWNTs with RuOEP. FET measurements were also performed for elucidation of the sensing mechanism by exposing the device to air or saturated vapors of acetone. The $I_{DS}-V_{DS}$ for the device was measured by linear sweep voltammetry using an electrochemical analyzer (CHI model 1202A, Austin, TX, USA) and FET measurement was done by using a semiconductor parameter analyzer (HP model # 4155A, Palo Alto, CA, USA). For FET measurements, the gold electrodes served as the drain and source while the aligned SWNTs/aligned modified SWNTs acted as the channel. The back-gate potential was applied through the highly doped Si surface. A 100 nm thick dielectric layer of SiO$_2$ was used to separate the back gate from the source-drain. The source-drain current ($I_{DS}$) was measured at room temperature as a function of applied gate voltage ($V_G$).

2.3 Results and discussion:

2.3.1 Verification of Porphyrin-SWNTs Hybrid Formation:

The formation of porphyrin-SWNT hybrid was verified by microscopy (SEM and AFM) and electrical ($I_{DS}-V_{DS}$ and $I_{DS}-V_G$, FET) studies of RuOEP-functionalized device. The Ru peak in the energy dispersive X-ray (EDAX) spectrum (Fig. 2.2a) of the corresponding SEM image (Fig. 2.1a, inset) confirmed the presence of Ru in RuOEP-
coated SWNTs. Similarly, the AFM analyses revealed an increase in the average diameter of the bare SWNTs from ~3.5 nm to ~7.5 nm after functionalization with RuOEP (Fig. 2.2b).

The modulation of resistance/conductance, threshold gate voltage, and transconductance of the SWNTs is a facile method for verifying functionalization of SWNTs. Figure 2.3 shows the $I_{DS}-V_{DS}$ and $I_{DS}-V_G$ (FET) characteristics of bare and RuOEP functionalized SWNTs. As shown in the Fig. 2.3a, the conductance of the bare SWNT device decreased significantly upon functionalization with RuOEP. Further, the RuOEP-coated SWNT device had a more negative threshold gate voltage ($V_{TH}$) and lower transconductance when compared with the bare SWNT device. These changes are attributed to the n-doping by the electron-donor porphyrin$^{21-23}$ of the p-type semiconductor SWNTs$^{2,3}$ that results in lower carrier (hole) concentration$^{21-23}$ (Fig. 2.3c) and carrier mobility (Fig. 2.3d).

2.3.2 VOCs Sensing:

To evaluate the potential of porphyrin-functionalized SWNT arrays for discriminating VOCs, room-temperature responses (defined as $\Delta R/R_0 \% = (R-R_0)/R_0 \times 100$; where $R =$ resistance of the device exposed to analyte and $R_0$ is the initial baseline resistance before analyte exposure) of various SWNT-porphyrin hybrid sensors as a function of concentration to a wide range of VOCs such as acetone, ethanol (EtOH), methanol (MeOH), methyl ethyl ketone (MEK), and dichloromethane (DCM), and water.
vapor were investigated.

Figure 2.4 illustrates a sample calibration plot along with the dynamic response (inset) of the SWNT-OEP hybrid for MEK detection. The data show a fast responding sensor with the response attaining 60% and 90% of the maximum in less than 1 and 7.2±1.9 min, respectively (Fig. 2.4, inset). Similar fast responses were observed for other porphyrin-functionalized SWNT devices with MEK and other VOCs tested (data not shown). Further, OEP-functionalized SWNT device was significantly more sensitive compared with the bare SWNT device. However, the improved sensitivity was not limited to SWNT-OEP and not all the porphyrin coatings improved the SWNTs’ sensitivity to MEK. As shown in Fig. 2.5, RuOEP-, FeOEP- and MnOEP-SWNT hybrid sensors were less sensitive, whereas OEP-, TPP-, RuTPP- and FeTPP-SWNT hybrid devices were more sensitive than the bare SWNT sensor for MEK. A similar non-selective response pattern was observed from porphyrin-functionalized SWNT hybrid sensors in the array for other VOCs tested in this work (Fig. 2.5). Thus, each analyte has a somewhat distinct response pattern/signature, making its identification/detection feasible by combining with chemometric analysis. The pattern/signature of each vapor can be attributed to the diversity of the sensing elements, that is, porphyrins, with different peripheral ligands and central metals. The exact role of the different functional groups of porphyrins in generating the signature is not well-understood and would require a more systematic investigation for elucidation. It is also worth noting that both RuOEP- and RuTPP-functionalized SWNT devices did not respond to water vapor, which should
be helpful for the success of sensor arrays in ambient environment where water vapor is present.

2.3.3 Sensing Mechanism:

The above sensing responses of porphyrin-SWNT hybrid devices can be ascribed to one or more of the following: electrostatic gating due to charge transfer, Schottky barrier modification resulting from work function change and reduced charge mobility by the introduced scattering sites.\textsuperscript{24} Reports in the literature on porphyrin-functionalized CNT devices for gas sensing proposed a charge transfer mechanism for the sensor response without any evidence.\textsuperscript{11,20} To shed light on the sensor mechanism, FET measurements were carried out for SWNT-RuOEP and SWNT-FeTPP upon exposure to dry air or saturated vapors of acetone. As evident from Fig. 2.6a, there was a negative shift of $\sim 5V$ of the threshold gate voltage ($V_{TH}$) with respect of air when SWNTs-RuOEP hybrid was exposed to acetone. Acetone is an electron-donating species, and thus, exposure to acetone causes a shift in the valence band away from the Fermi level, resulting in a decrease in charge carrier (hole) concentration\textsuperscript{25} ($\sim 3.3 \times 10^{10} \text{ cm}^{-1}$), thereby causing a reduction in conductivity and negative shift in the threshold voltage ($V_{TH}$) of the device. In comparison, the mobilities (calculated from the device transconductance, slope of the $I_{DS}$ vs. $V_G$) of the SWNT-RuOEP device in air, and saturated acetone were $\sim 3.6 \times 10^{-2}$ and $\sim 4.1 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively.\textsuperscript{26} Thus, the change in $V_{TH}$ as well as carrier concentration is significant in magnitude when compared to mobility for acetone, indicating that the sensing mechanism for the SWNT-RuOEP hybrid is governed by
electrostatic gating effect.  

Figure 2.6b shows the FET transfer characteristics for the FeTPP-functionalized SWNT device. Once again, like SWNT-RuOEP, a negative shift in of 11.4 V in the gate voltage with respect to air was observed upon exposure to saturated vapors of acetone. This corresponds to a carrier concentration change of $\sim 2.8 \times 10^{10}$ cm$^{-1}$ in acetone environment compared with air. However, unlike the SWNT-RuOEP device, there was a significant change in the mobility of the SWNT-FeTPP upon exposure to acetone ($\sim 4.9$ cm$^2$V$^{-1}$s$^{-1}$) compared with air (1.1 cm$^2$V$^{-1}$s$^{-1}$). This 4-fold change in mobility indicates a decrease in work function of the device on absorption of analyte gas at the gold contact, causing Schottky barrier modulation.  

Thus, a threshold voltage shift and mobility change in case of SWNT-FeTPP hybrid device suggests that the sensing mechanism is governed by electrostatic gating and Schottky barrier effect in combination.

2.3.4 Principal Component Analysis:

To evaluate the VOC identification performance of porphyrin-SWNT hybrid sensor arrays, the simple statistical chemometric technique of principal component analysis (PCA) was used. A data matrix was constructed whose columns were the peak responses from seven sensors (SWNTs, SWNT-OEP, SWNT-RuOEP, SWNT-FeOEP, SWNT-TPP, SWNT-RuTPP, and SWNT-FeTPP) and the rows represented measurements for each gas. For each gas, three measurements (corresponding to 100%, 75% and 50% saturated vapors) were selected. Thus, the data matrix had 15-rows and 7-columns. Multivariate analysis was carried out performing principal component
analysis (PCA). PCA is an orthogonal projection of data from a higher dimensional space to a lower dimensional one such that the variance of the projected data is maximized. In our case, we found that first three principal components (PCs) accounted for ~88% of the variance. Visual analysis was enabled by plotting the scores: the projection of the data points in the PC space. The first principal component (PC1) contained information about the concentration of the analyte. As shown in Fig. 2.7a, the concentration of each analyte increased as the magnitude of PC1 increased and followed a definite trend between different concentrations of analytes. Further, the PCA plot of the second (PC2) and third principal components (PC3) provided information about the discriminatory power of the sensors. It can be observed from Fig. 2.7b that the scores representing each gas were clustered together and there was a clear separation between the clusters corresponding to each gas.

2.4 Conclusions:

To summarize, we have fabricated single-walled carbon nanotube-porphyrin hybrid based chemiresistive nanosensor arrays for monitoring toxic substances in the environment. Differences in sensing performance are observed for porphyrins with different functional groups and with different central metal atoms. Free-base and metal (e.g. ruthenium and iron) substitution with octaethyl and tetraphenyl porphyrins provide good selectivity and sensitivity to various VOCs tested. The FET analysis revealed that the sensing mechanism of the SWNT-RuOEP device is governed by electrostatic gating.
effect, and for SWNT-FeTPP device it is electrostatic gating and Schottky barrier modulation in combination. However, Schottky barrier modulation is dominant over the electrostatic gating effect in case of SWNT-FeTPP device. Further, the test data generated by the hybrid nanosensor arrays were analyzed using the PCA technique. PCA analyses confirmed the presence of a definite pattern in response data for different hybrid materials and the ability to differentiate analyte from one another. This discriminating power of the hybrid devices and availability of the wide range of commercially available synthetic porphyrins open up an opportunity to develop a highly dense nanosensor array for E-nose applications.
2.5 References:


Figures:

Figure 2.1 Schematic representation of the gas sensing system
Figure 2.2 (a) Energy-dispersive X-ray analysis (EDAX) spectrum and SEM image of RuOEP-coated SWNTs (inset). (b) Height distribution of bare and SWNT-RuOEP devices obtained from AFM analysis.
Figure 2.3 Electrical and FET transfer characteristics of bare and RuOEP-functionalized SWNT device: (a) $I_{DS} - V_{DS}$ curve (at $V_{GS} = 0$ V), (b) $I_{DS} - V_{GS}$ curve (at $V_{DS} = -1$ V), (c) carrier concentration vs. resistance curve and (d) carrier mobility vs. resistance curve.
Figure 2.4 Calibration curve of MEK for bare SWNT and OEP functionalized devices and transient response of MEK for SWNT-RuOEP device (inset).
Figure 2.5 Histogram showing comparison of responses of bare and free-base and metal-substituted porphyrin functionalized devices towards acetone, methanol, ethanol, MEK and water (@100% saturated vapors).
Figure 2.6 Transfer characteristic ($I_{DS} - V_{GS}$ curves at $V_{DS} = -1$ V) of (a) SWNT-RuOEP and (b) SWNT-FeTPP devices in presence of air and saturated vapors of acetone.
Figure 2.7 (a) PCA plot (PC1 vs. PC2) of scores using seven sensors (bare SWNT, SWNT-OEP, SWNT-RuOEP, SWNT-FeOEP, SWNT-TPP, SWNT-RuTPP, and SWNT-FeTPP) and (b) PCA plot (PC2 vs. PC3) of seven sensors showing well-separated clusters for four VOCs tested (MeOH, EtOH, MEK and acetone).
CHAPTER 3

Single-Walled Carbon Nanotube-poly(Porphyrin) Hybrid for Volatile Organic Compounds Detection

Abstract

Porphyrins have been widely investigated as functional materials for chemical sensor fabrication due to their unique and interesting physicochemical properties. However, the poor conductivity of porphyrins is a major limitation towards the porphyrin-based chemiresistor sensor development. The conductivity issue could be resolved by exploiting the excellent electrical properties, in particular the higher charge carrier mobility, of single-walled carbon nanotubes (SWNTs) and thus making a SWNT-based hybrid device, where SWNT would act as a transducer and porphyrin would act as a sensory layer. The hybrid could be fabricated through simple adsorption of porphyrin on the SWNT. However, the adsorption method results in only a partial surface coverage of the SWNTs and therefore incomplete realization of the full sensing potential. Full surface coverage of the SWNTs with porphyrin could be achieved through electropolymerization of porphyrin. The present attempt is to fabricate a SWNT-poly(tetraphenylporphyrin) hybrid through electrochemical routes and to evaluate the potential of that hybrid for the development of a low-power chemiresistor for volatile organic compounds detection. Various charge densities were applied to get different
thicknesses of porphyrin polymer on SWNT to tune the hybrid properties and the electrochemical process provides the process flexibility. Differences in sensing performance were noticed for the hybrid fabricated at various charge densities and the optimum-sensing response was found at 19.65 mC/cm$^2$. The hybrid exhibited a wide dynamic range of acetone vapor sensing from 50 to $\sim$23,000 ppm with a limit of detection of 9 ppm. They also showed a significant response towards benzene, toluene, ethylbenzene and xylenes starting from 1.25 ppm of analyte exposure with a sub ppm limit of detection. The field-effect transistor studies showed a negative threshold voltage shift and almost constant transconductance when exposed to air/analyte, which indicate that the sensing mechanism to be dominated by the electrostatic gating effect. Further, the results confirmed a good stability of the device over a period of 180 days. This long term device stability along with the sensing capability at low analyte concentration with a wide detection range and easily scalable fabrication technique signify the potential of SWNT-poly(porphyrin) hybrid for volatile organic compound sensing applications.
3.1 Introduction:

Porphyins are organic, macrocyclic compounds having interesting chemical and optical properties as well as good chemical stability. Its ability to interact with the analyte molecule through weak van der Waal forces and coordination interaction with the inner core metal ion\(^2\),\(^3\) and the measurable physical property change upon porphyrin-analyte binding make them an attractive class of sensing materials. The sensing capabilities of porphyrin have been explored based on optical\(^4\)-\(^6\) and mass detection.\(^7\),\(^8\) Porphyrin has also been used as a colorimetric sensor for toxic gas detection.\(^9\) The device fabrication and the transduction mechanism of colorimetric and optical sensors are simple. However, (1) high power requirement, (2) limited sensitivity, (3) lower dynamic range, (4) large volume of the total sensor assembly and (5) higher initial cost limit the use of these devices for mobile/field-deployable applications. An attempt has been made to fabricate thin film based field-effect transistors (ChemFET) via immobilization of porphyrin on a discontinuous gold film.\(^10\) However, Porphyin thin film based ChemFET needed multiple steps to fabricate and they also showed limited sensor sensitivity. They also need higher power to operate. In this regard, chemiresistive sensors based on conductivity changes could be easier to fabricate, which would needed less number of steps and they could also be operate at low power. However, very low electrical conductivity of the porphyrin structure restricts its use for only porphyrin-based chemiresistive sensor development.\(^11\)

On the other hand, single-walled carbon nanotubes (SWNTs) have unique electrical\(^12\),\(^13\) and structural\(^14\) properties, leading to usability in diverse applications. Its
nanometer range dimensions enable fabrication of high-density sensor device within a limited space. In particular, high electrical mobility, which facilitates fabrication of low power device and the property of conductance change upon adsorption of analyte gas molecules make SWNTs a promising material for sensor development.$^{15-17}$ However, lack of sensor performance in terms of sensitivity and selectivity is intrinsic in carbon chemistry and it limits the use of SWNTs as an individual sensor.$^{18}$ This problem could be alleviated, to a certain degree, through surface modification of SWNT with a suitable molecular recognition system.$^{19-21}$ Surface modification of SWNT with various materials like polymers$^{21,22}$, metals$^{23}$ and metal oxides$^{24}$ have been reported to improve the sensing performance of the device towards various analyte gases. This strategy of surface functionalization towards the enhancement of sensor performance facilitates the possible development of SWNT-porphyrin device, exploiting both the binding ability of porphyrin with the analyte and the electrical properties of SWNTs. In this device, the binding ability of the porphyrins with different analytes contributes towards the improvement of sensor performance and the high electrical mobility of SWNTs facilitates to make low power chemiresistive sensor by improving the device conductance.

There are reports on multi-walled carbon nanotube (MWCNTs) based porphyrin sensor for volatile organic compound (VOCs) detection.$^{3,25}$ The MWCNT-porphyrin device was fabricated by using solvent casting techniques where porphyrin was noncovalently attached on the carbon nanotube surface through $\pi-\pi$ interaction without much change in carbon nanotube electronic properties.$^{26}$ However, this method results in only partial surface coverage of SWNTs and thus incomplete realization of the full
sensing potential.\textsuperscript{11} Full surface coverage of SWNTs with porphyrins could be achieved through the electropolymerization of porphyrin.

In this work, we report SWNT-based hybrid nanostructure, fabricated through electrochemical polymerization of tetraphenylporphyrin (TPP) on SWNT network and evaluate the potential of this nanostructure as a chemiresistive sensor for acetone, and other volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene and xylenes (commonly known as BTEX compounds). The nanostructures were characterized using scanning electron microscopy (SEM), Raman spectroscopy, attenuated total reflectance (ATR)-infrared spectroscopy (IR), current-voltage (I-V) and field-effect transistor (FET) measurement. The electrochemical process optimization was done through sensing performance evaluation of the hybrid fabricated at different process conditions. The electrical characterization through field effect transistor (FET) measurement of the hybrids prepared at various process conditions enables us to understand the relationship between the fabrication process parameters and the electrical properties of the hybrid, and provide an insight about the process optimization. Further, systematic study of sensing performance evaluations reveals a several fold increase in sensitivity of the hybrid as compared to porphyrin functionalized SWNTs, wide dynamic range and long-term device stability. FET measurements at various BTEX concentrations indicate that the sensing mechanism is governed by charge transfer or dominated by electrostatic gating effect.
3.2 Experimental Details:

3.2.1 Nanosensor Fabrication:

SWNT suspension was prepared dispersing 0.1 mg of carboxylated SWNTs [P3 SWNT-COOH, 80-90% purity from Carbon Solution Inc. (Riverside, CA)] in 10 ml of N,N-dimethylformamide (DMF) (Sigma Aldrich, Spectral grade) by ultrasonication for 90 minutes. The suspension was then centrifuge at 31000g for another 90 minutes to separate soluble fractions from the aggregates. The separated soluble fraction of SWNT was used for device fabrication.

Sensor electrodes were micro-fabricated on highly doped p-type silicon substrate by standard lithographic patterning. An approximately 300 nm thick dielectric layer of SiO$_2$ was first grown on the Si-substrate by low-pressure chemical vapor deposition (LPCVD). The interdigitated electrodes (electrode finger L X W: 100 µm X 5 µm, gap between each finger: 3 µm, total number of fingers: 20) were then written on the SiO$_2$/Si substrate using photolithography, followed by the deposition of a 20 nm thick Cr layer and a 180 nm thick Au layer by e-beam evaporation, and finally the electrodes were defined using a standard lift-off processes.

SWNTs were aligned across the Au-electrodes gap via dielectrophoretic (DEP) alignment by placing a 0.2 µL drop of SWNT-suspension on top of the electrode gap, applying 3 V$_{pp}$ at a frequency of 4 MHz by a function generator (Wavetek, San Diego, CA). The resistance of the device could be adjusted by varying the SWNTs concentration in the suspension and/or the deposition time. After alignment, the electrode was then annealed at 300 °C for 90 min in a reducing environment (5% H$_2$ in N$_2$). The annealing
process improved the contact between the Au-pad and the SWNTs by removing any possible residual DMF between the Au-pad and the SWNTs.

3.2.2 Electrochemical Functionalization:

Electrochemical functionalization of SWNTs with tetraphenylporphyrin polymer was conducted at room temperature by using a three-electrode electrochemical cell configuration. The SWNT network on gold electrode was used as a working electrode (WE). One of the gold electrodes, without the SWNT network was used as a counter electrode (CE) and a silver wire in AgNO$_3$ (Ag / AgNO$_3$ (0.02 M) in acetonitrile) was used as a reference electrode (RE). Electropolymerization was done by potentiostatic electrodeposition at +2V versus Ag/AgNO$_3$ using a deoxygenated electrolytic solution of 0.2 M tetrabutylammonium perchlorate (TBAP) and 2 mM of tetraphenylporphyrin (TPP) in dichloromethane (CH$_2$Cl$_2$). The deposition was done for a fixed charge. After electropolymerization, the device was rinsed several times with CH$_2$Cl$_2$ followed by nanopure water and finally dried with nitrogen gas.

A custom made electrochemical cell (Figure 3.1) was used for electropolymerization. The prefabricated electrode was designed according to the dimensions of the electrochemical cell. The compatibility issue between the cell and the electrode was taken care of in a cautious manner so that while inserting the electrode into the cell, the electrode area exposed to the electrolyte was constant every time. During the electropolymerization process, the polymer growth occurs on the SWNT network as well as on the gold surface exposed to the electrolyte. The charge density of electropolymerization was computed based on the gold electrode area exposed to the
electrolyte as the total surface area of the SWNTs network is negligible with respect to the surface area of the gold electrode exposed to the electrolyte.

3.2.3 Characterizations:

The nanostructure characterization was done by using scanning electron microscope (SEM), atomic force microscope (AFM), Raman spectrometer and attenuated total reflectance (ATR)-IR spectrometer. SEM images were obtained using Zeiss Leo SUPRA 55 with beam energy of 20 kV. AFM images were taken using a Veeco Innova AFM. Raman spectra were collected in Nicolet Almega XR Dispersive Raman microscope with a 0.7 µm spot size and 532 nm laser excitation. The ATR-IR spectra were taken using a Thermo Nicolet Nexus 670 FTIR instrument equipped with an ATR sampling accessory.

Electrical characterization was done using a semiconductor parameter analyzer (HP model no. 4155A) through current-voltage (I-V) measurements and FET measurements to confirm surface functionalization of SWNTs. FET measurements were also performed to understand the effect of the tetraphenylporphyrin polymer thickness on the electrical properties of the hybrids and to elucidate the sensing mechanism by exposing the hybrid to air or various concentrations of BTEX vapor. During FET measurements, the gold electrodes served as the source and the drain while the aligned SWNTs/SWNTs-poly(TPP) hybrid acted as the channel. The back gate potential was applied through the highly doped Si substrate. A dielectric layer of 300 nm thick SiO₂ was used to separate the back gate from the source-drain. The fixed potential of 1 V was applied between the source and the drain while the gate voltage was swept from -40 to 40
V. The source-drain current ($I_D$) was recorded at room temperature as a function of the applied gate voltage ($V_G$). The device and the measurement apparatus were also carefully grounded to reduce electronic noise.

3.2.4 Gas sensing studies:

An indigenous sensing platform (Figure 3.2) was designed to perform the gas-sensing studies. During measurement, a bias potential of 1 V was applied across the sensor, and the resistance of the device was recorded with respect to time. For this purpose, a Keithley 2636 dual-channel system source-meter was used. A multiplexer connected to the source-meter was used for simultaneous measurement of all the sensors. A LabView program was developed in-house and was used to control the entire process. To link up the sensor with the source-meter, it was first wire-bonded to a chip holder and then connected with the multiplexer through a breadboard. The sensor was covered with a 13 cc sealed glass dome with a gas inlet and outlet. Dry air (purity: 99.998%, Air gas Inc. Riverside, CA, USA) was used as carrier gas. Saturated VOCs vapor was generated by passing dry air through a bubbler filled with liquid VOCs. Different concentrations of analyte vapor were obtained by mixing the vapor stream with dry air. A series of mass flow controllers (Alicate Scientific Inc, Tucson, AZ) were used to control the gas flow rate and to achieve the desired analyte concentration. In all the experiments, sensors were first exposed to dry air to achieve the baseline followed by a desired concentration of analyte vapor concentration and then back to air, which completed one cycle.
3.3 Results and Discussion:

To determine the electropolymerization working potential of TPP, cyclic voltammogram (CV) was conducted at room temperature on a standard gold disk electrode (2 mm diameter) and a SWNT spray coated gold disk electrode in a deoxygenated electrolytic solution of 0.2M tetrabutylammonium perchlorate (TBAP) and 2 mM of tetraphenylporphyrin (TPP) in dichloromethane (CH$_2$Cl$_2$). In both cases, the anodic oxidation potential for TPP electropolymerization was found to be around 2V vs. Ag/AgNO$_3$, which is very close to the previously reported value of 1.95 V (Figure 3.3). The CV indicated that the electropolymerization of TPP on SWNTs started when the applied deposition potential became or was more positive than 2V (vs. Ag/AgNO$_3$). Based on this information, future electropolymerization was performed at a constant potential of 2V (vs. Ag/AgNO$_3$) to fabricate SWNT-poly(TPP) hybrid.

Schematic representation of the SWNT-poly(TPP) hybrid fabrication steps are shown in Figure 3.4. During the oxidative electropolymerization process, the TPP monomer loses three electrons one at a time starting with the formation of radical-cation [TPP$^+$] followed by dication [TPP$^{2+}$] formation and finally converted into radical-cation [(TPP$^{2+}$)$^•$]. This active radical-cation, [(TPP$^{2+}$)$^•$] then binds covalently either with the side-walls of the SWNTs via C-C bond formation (SWNT-aryl bond) or reacts with another [(TPP$^{2+}$)$^•$] through aryl-aryl couplings to produce a TPP polymer. However, first, the covalent attachment of porphyrin with the SWNTs is expected because of the radical formation at the electrode surface i.e., SWNTs, during the electrochemical process and later, polymerization of porphyrin is expected on top of the covalently
modified SWNTs, which provides an extra layer of porphyrin polymer on the SWNT surface. The SEM images of the bare (Figure 3.5a) and electrochemically modified (Figure 3.5b) SWNTs revealed a uniform coating all over the surface and an increase in diameter of the SWNTs due to porphyrin polymeric coating. To get an insight into this surface functionalization, Raman spectroscopy was performed. A sharp $G^-$ (1564 cm$^{-1}$) and $G^+$ (1588 cm$^{-1}$) peak, which is the characteristic signature of SWNTs, along with a small D-peak (1340 cm$^{-1}$) due to the presence of carboxyl group at the sidewall of the SWNTs, were evident in the Raman spectra (Figure 3.5c).\textsuperscript{29} A significant enhancement in $I_D/I_G$ ratio as compared to SWNTs and an overlapping of $G^-$ and $G^+$ peak were observed for SWNT-poly(TPP) hybrid, whereas, no significant change in $I_D/I_G$ ratio was noticed for non-covalently functionalized SWNT-TPP (Figure 3.5c). This enhancement of $I_D/I_G$ ratio is attributed towards the increase in defects on SWNTs due to the covalent attachment of the TPP radical to the SWNT, which creates a new sp$^3$ carbon center in place of an sp$^2$ carbon atom in the SWNT lattice.\textsuperscript{30, 31} An increase in resistance (∼few hundred folds) (Figure 3.5d) along with an increase in $I_{on}/I_{off}$ ratio (∼3 folds) (Figure 3.5e) due to the delocalization of sp$^2$ carbon center and formation of sp$^3$ carbon center in SWNT-poly(TPP) hybrid are also in agreement with the Raman spectra results. On the other hand, the Raman spectra of SWNTs and non-covalently modified SWNT-TPP look alike without any observable change in the $I_D/I_G$ ratio, which is in agreement with the previous report.\textsuperscript{32}

The formation of TPP polymer on SWNT was further confirmed by attenuated total reflectance (ATR)-IR spectroscopy (Figure 3.5f). The spectrum of SWNT-
poly(TPP) shows the characteristic band at about 845, which is ascribed to the out-of-plane CH wagging vibration of the biphenyl group formed due to aryl-aryl coupling.\textsuperscript{33}

SWNT-poly(TPP) hybrids were fabricated by applying various charge densities to achieve different TPP polymer thicknesses on SWNTs network and the device performance was evaluated on the basis of sensing performance towards various acetone vapor concentrations. An increase in resistance was observed upon exposure to acetone. A typical dynamic response of the hybrid devices prepared at various charge densities is shown in Figure 3.6a in terms of normalized resistance change \((\Delta R/R_o \% = (R-R_o)/R_o \times 100)\); where \(R\) is the resistance of the hybrid exposed to analyte and \(R_o\) is the initial base line resistance before analyte exposure. From these dynamic response data, the sensing response of the SWNTs-poly(TPP) hybrid was computed and plotted as normalized resistance change with respect to the charge density applied during electropolymerization (Figure 3.6b). It shows, with the increase of charge density, the sensing response of the device improves for all concentrations of acetone vapor and reach a maximum at 19.56 mC/cm\(^2\) and then decrease with the increase in charge density. During electropolymerization, with the increase of applied charge density, more number of porphyrin units will polymerize and provide increased thickness of (poly)porphyrin coating on SWNT. Further, with the increase of polymer thickness, more porphyrins units will be available to interact with the analyte molecule and an enhanced the sensing response is expected. However, with the increase of polymer thickness on SWNTs, the hybrid would become more insulating due to the low conductivity of the porphyrins, which may hinder the charge transfer process and may cause a decrease in sensing
performance after achieving an optimum value. To get an insight into this fact, FET studies were done for all hybrid devices prepared at different charge densities.

During FET measurements, the hybrids prepared at various charge densities acted as the channel. Figure 3.7a presents a typical transfer characteristic ($I_D - V_G$) curve of the hybrid device prepared at a charge density of 23.59 mC/cm$^2$ upon exposure to air and saturated acetone vapor. A negative shift in threshold voltage ($V_{G,T}$) and almost no change in transconductance with respect to air were observed. The change in carrier concentration was computed from the change in $V_{G,T}$ with respect to air and the change in mobility was computed from the transconductances. The mobility of the hybrid device was calculated assuming the MOSFET linear region model using the equation

$$\mu = g_m \times \frac{L^2}{C_G} \times \frac{1}{V_D},$$

where $\mu$ is the carrier mobility, $\frac{g_m}{W}$ is the normalized transconductance of the device $\left(\frac{\partial I_D}{\partial V_G}\right)$, $W$ being the channel width, $L$ is the channel length (3 $\mu$m) and $V_D$ is the drain voltage (1 V). The gate capacitance ($C_G$) can be computed using the equation

$$C_G = \varepsilon_o \varepsilon_d W \frac{L}{L_{OX}},$$

where $\varepsilon_o$ is the permittivity of free space, $\varepsilon_d$ is the dielectric constant of SiO$_2$ and $L_{OX}$ is the thickness of the dielectric layer (300 nm). The carrier concentration ($n$) can be computed using the equations $n = \frac{Q}{\varepsilon L}$ and $Q = C_G \times V_{G,T}$. The threshold voltages, $V_{G,T}$, were computed from transfer characteristics by extrapolating the linear portions of the curves to zero current and the transconductances were computed from the slope of the linear portions of the curves.
Since the device resistance varies widely depending on the charge density applied during the fabrication, the transfer characteristics of the hybrid devices prepared at various charge densities were computed in terms of normalized drain current ($I_{D,\text{normalized}}$) from the individual device transfer characteristics and plotted as a function of gate voltage ($V_G$) (Figure 3.7b). The current ($I_D$) measured at -40 V gate potential ($V_G$) in air is considered as the basis for normalizing the source-drain current in the transfer characteristics curves.

Further, carrier concentration was computed from $I_{D,\text{normalized}}-V_G$ curves of the individual devices and plotted in terms of normalized change carrier concentration ($-\Delta n/n_o$) as a function of charge density (Figure 3.7c), where $n_o$ indicates the carrier concentration of the hybrid device in air medium and $n$ indicates the carrier concentration in presence of saturated acetone vapor. The mobilities of the devices were also computed from the transconductance and plotted in terms of normalized mobility change ($\Delta \mu/\mu_o$) as a function of charge density (Figure 3.7d). No significant change in $\Delta \mu/\mu_o$ was observed with respect to applied charge density during the SWNTs hybrid fabrication (Figure 3.7d). However, $-\Delta n/n_o$ versus charge density plot (Figure 3.7c) showed a similar trend as $\Delta R/R_o$ versus charge density plot (Figure 3.6b). This behavior confirms that the thickness of porphyrin polymer makes the hybrid more resistive and restricts the charge transfer process during the interaction with the analyte, thus resulting in the decrease in carrier concentration and the sensing performance of the hybrid when it is fabricated by applying more than the optimum charge density (19.65 mC/cm²).

Structural characterization of the hybrid device fabricated at optimized charge density was done by AFM analysis. AFM image (before and after functionalization with
TPP polymer) along with the line scan confirm an almost uniform coating on SWNT network and an increase in height for each SWNT after coating (Figure 3.8a). From the AFM images, the height distribution as a function of SWNTs diameter was derived and plotted in Figure 3.8b. The height distribution plot reveals an increase in thickness of the average diameter of bare SWNTs from ~3 to ~7 nm after electropolymerization of TPP on SWNT network.

The sensing performance evaluation of SWNT-poly(TPP) hybrid prepared at optimized charge density was done by exposing it to various acetone concentrations and comparing with the sensing results obtained from bare SWNTs as well as TPP functionalized SWNT (SWNT-TPP) devices. SWNT-TPP was fabricated using solvent casting techniques. A higher concentration of acetone (12.5, 25 and 50% saturated vapors of acetone) was used during sensing experiment for the purpose of performance comparison, as SWNT sensitivity towards low concentration of acetone is not significant. Figure 3.9a shows the comparison of dynamic responses of these sensors. An increase in resistance was observed for all the devices upon exposure to acetone vapor. Average response times (time required to achieve 90% of the response) of ~12 minute for bare SWNTs, ~10 minutes for SWNTs-TPP, and ~8 minutes for SWNTs-poly(TPP) devices were computed from the dynamic response curves. An improvement in sensor recovery was also noticed for SWNT-poly(TPP) hybrid as compared to the bare and TPP functionalized SWNTs devices. Figure 3.9b, the calibration curve, established the fact that the coating of SWNTs with TPP polymer enhances the sensing response several folds higher than bare SWNTs as well as SWNT-TPP devices. These sensing results

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encouraged to perform further sensing experimentation at lower concentrations of acetone to evaluate the actual potential of the SWNTs-(poly)TPP hybrid devices. The experiment was performed from 50 ppm, which is 5% of the OSHA (Occupational Safety and Health Administration) PEL (Permissible Exposure Limits) concentration to 2000 ppm, which is twice the OSHA PEL value of acetone vapors (OSHA PEL of acetone is 1000 ppm). A typical real time sensing response is shown in Figure 3.10a. A sharp increase in resistance upon each exposure of acetone concentration and a quick recovery of the device were noticed. Figure 3.10b shows the calibration curve of the same and can be fitted by a Langmuir-like adsorption isotherm, where the relationship between the normalized resistance change \((\Delta R / R_o)\) and the concentration \(c\) is governed by the equation

\[
\frac{\Delta R}{R_o} = \left(\frac{\Delta R}{R_o}\right)_{\text{max}} \cdot \frac{c}{k + c}
\]

where \((\Delta R / R_o)_{\text{max}}\) is the maximum change in normalized resistance occurring in the saturation regime, and \(k\) is the affinity constant. Figure 3.10b(i) represents the absorption isotherm curve, which can be drawn on the basis of experimental data with a \(R^2\) value of 0.96. The constants \((\Delta R / R_o)_{\text{max}}\) and \(k\) values were computed from the absorption isotherm and found to be 10.62 and 49.15 respectively. The sensitivity \(S\) of the sensor was computed by using the equation

\[
S = \frac{d\left(\frac{\Delta R}{R_o}\right)}{dc} = \left(\frac{\Delta R}{R_o}\right)_{\text{max}} \cdot \frac{k}{(k + c)^2}
\]

at low concentrations \((c \to 0)\). The sensitivity of the device was calculated to be \(\sim 0.22\) % per ppm of acetone vapor. Although this isotherm can justify most of the results obtained at the lower concentration range of the
experiment, a significant deviation was also observed at the higher concentration range. However, the response of the entire concentration range of the calibration curve can be well explained with two different straight lines, which can be best fitted separately, one in the lower and another in the higher concentration range. Lower concentration range data can be fitted by the equation \( \frac{\Delta R}{R_o} = 0.08c \) with a \( R^2 \) value of 0.95 (Figure 3.10b(ii)) and the limit of detection (LOD) can be computed using this equation. LOD was computed considering a real signal, which is three times greater than the signal to noise, and was found to be \( \sim 9 \) ppm of acetone vapor. The higher concentration range data can be well represented by the equation \( \frac{\Delta R}{R_o} = 0.006c + 9.8 \) with a \( R^2 \) value of 0.96 (Figure 3.10b(iii)) and this equation justifies the results obtained from the saturated acetone vapor sensing (Table 3.1) experiment. Further, to check the stability of the hybrid, the sensing performance was evaluated at 50 % saturated vapors of acetone in a regular interval for a period of six months. From the real time sensing data (Figure 3.11a), the normalized resistance change (\( \Delta R/R_o \)) was computed and plotted as a function of number of days. An initial decrease in performance was observed during the initial period, however, there was no significant change in performance after 60 days (Figure 3.11b). The devices were stored under vacuum when not in use during stability check experimentation.

The sensing performance evaluation of the SWNT-poly(TPP) device was also done by exposing it to various concentrations of for BTEX vapors ranging from 1.25 to 15 ppm. Figure 3.12a shows the real time sensing response of the device towards benzene in terms normalized resistance change. Like acetone, an increase in device resistance was
also observed when exposed to benzene as well as other BTEX vapors. No response was observed towards benzene and other BTEX vapors (data not shown) for bare SWNT devices. The calibration curves of BTEX, shown in Figure 3.12b, indicate a nonlinear behavior which is similar to the acetone response at lower concentration. The limit of detection (LOD) of benzene was calculated from the liner range of the calibration curve (Figure 3.12c) considering a real signal equal to three times the signal-to-noise ratio. LOD calculation for the other BTEX compounds was also done by applying similar rule that was applied for the LOD calculation of benzene. The sensitivity and the LOD of the sensor for BTEX compounds are summarized in Table 3.2. It is evident that the hybrid provides a significant sensing response at a concentration of 1.25 ppm for all BTEX vapors (Figure 3.12b). The calculated LODs for BTEX vapors were also found to be sub ppm level, which are well below their OSHA PEL (OSHA PEL for benzene, toluene, ethylbenzene and xylenes are 1, 200, 100 and 100 ppm, respectively).

In order to have an understanding about the sensing mechanism, FET measurements were carried out for SWNT-poly(TPP) hybrid device upon exposure to dry air or 15 ppm of the BTEX vapor concentration. A negative shift of the threshold voltage ($V_{TH}$) and insignificant change in transconductance ($dI_D/dV_G$) with respect to air were observed when exposed to BTEX vapors (Figure 3.13). BTEX are electron-donating species, hence on adsorption these analytes donate electrons to the surface of the p-type SWNT device resulting in a decrease in carrier (hole) concentration, thereby causing a negative shift in $V_{TH}$ and reduction in conductivity of the device. Thus, the significant change in $V_{TH}$ and almost no change in $dI_D/dV_G$ indicate that the sensing mechanism is
governed by electrostatic gating effect.\textsuperscript{36} It is noteworthy that the change in $V_{TH}$ upon analyte exposure is in agreement with the sensing result shown in Figure 3.12b.

**3.4 Conclusions:**

In summary, we have fabricated single-walled carbon nanotube-poly(porphyrin) hybrid through electrochemical route and have evaluated the sensing potential. The process flexibility of the electrochemical technique allows getting various thicknesses of tetraphenyl porphyrin polymer on SWNTs by controlling the charge density to tune the hybrid properties. During electropolymerization, an increased charge density provides an increased polymer thickness and makes more amount of porphyrin available to interact with the analyte, which enhances the sensing performance. However, results indicate that the sensing performance increases up to an optimum charge density of 19.56 mC/cm$^2$ after which device performance decreases. FET analysis reveals that the properties of the hybrids prepared at more than the optimum charge density are dominated by the higher resistance of the hybrid, which could restrict the charge transfer process during interaction with the analyte and thus cause a decrease in charge carrier density that results in a decrease in sensor response. Further, AFM analysis revealed that the TPP polymer coats the SWNTs uniformly with the thickness of the film being $\sim$4 nm when prepared at optimum condition.

Results indicate that the hybrid device fabricated at the optimum condition shows about a four-fold increase in sensitivity towards acetone as compared to bare and TPP
functionalized SWNT device. The sensitivity of the sensors, calculated from the sensing results, follows Langmuir like isotherm is \( \sim 0.25 \% \) per ppm of acetone vapor. The limit of detection was calculated to be \( \sim 9 \) ppm for acetone sensing. A wide dynamic range from 50 ppm to \( \sim 230,000 \) ppm of acetone vapor was also observed for SWNT-poly(TPP) hybrids. Results were also indicating that the sensor was able to detect BTEX vapor down to 1.25 ppm concentration. A sub ppm level LOD was found for BTEX compounds, which is well below their OSHA PEL level. Further, the FET analysis at various exposures to BTEX vapor revealed that the sensing mechanism of SWNT-poly(TPP) device is governed by electrostatic gating effects. The hybrids also provide a fairly stable sensing performance until 180 days. The ability of analyte detection well below OSHA PEL level, wide dynamic range, long-term stability, scalable fabrication techniques, and availability of various types of synthetically derived porphyrins, which can provide different sensitivity towards various VOCs, make SWNT-poly(porphyrin) hybrid a potential material for further array based sensor development.
3.5 References:


Tables:

<table>
<thead>
<tr>
<th>% Saturated vapors of acetone</th>
<th>Corresponding concentration of the saturated vapors of acetone in ppm [calculated using Antoine equation @ 25 °C]</th>
<th>Sensing response ($\Delta R/R_0$ / %) computed by using the equation, $\Delta R/R_0 = 0.006c + 9.8$</th>
<th>Sensing response ($\Delta R/R_0$ / %) obtained during saturated acetone vapor sensing experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>$\sim 233,000$</td>
<td>$\sim 149$</td>
<td>$139 \pm 13$</td>
</tr>
<tr>
<td>25</td>
<td>$\sim 116,000$</td>
<td>$\sim 80$</td>
<td>$69 \pm 11$</td>
</tr>
<tr>
<td>12.5</td>
<td>$\sim 58,000$</td>
<td>$\sim 45$</td>
<td>$34 \pm 8$</td>
</tr>
</tbody>
</table>

**Table 3.1** Comparison of the sensor response calculated from the fitted equation and experimental results.
<table>
<thead>
<tr>
<th>Analyte</th>
<th>$[\Delta R/R_0]_{\text{max}}$</th>
<th>K / ppm</th>
<th>Sensitivity / ppm$^{-1}$</th>
<th>Limit of detection / ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>18.74</td>
<td>12.01</td>
<td>1.56</td>
<td>~ 600</td>
</tr>
<tr>
<td>Toluene</td>
<td>30.41</td>
<td>14.63</td>
<td>2.08</td>
<td>~ 500</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>31.19</td>
<td>12.73</td>
<td>2.45</td>
<td>~ 375</td>
</tr>
<tr>
<td>Xylenes</td>
<td>25.99</td>
<td>7.07</td>
<td>3.67</td>
<td>~ 200</td>
</tr>
</tbody>
</table>

**Table 3.2** Room temperature values of the constants $[\Delta R/R_0]_{\text{max}}$ and k, sensitivity and LOD of the SWNT-poly(TPP) hybrid for BTEX.
Figures:

Figure 3.1 Schematic representation of the custom made electrochemical cell
Figure 3.2 Schematic diagram of the gas sensing setup.
Figure 3.3 Cyclic voltammetry in CH$_2$Cl$_2$ (TBAP 0.2M) in presence of tetraphenyl porphyrin (H$_2$TPP)(2 mM), one cycle from -1.9 to 2.4 V at a scan rate of 100 mV/s; working electrodes: gold disk and SWNT spray coated on gold disk; reference electrode: Ag/AgNO$_3$ (0.02 M) in acetonitrile; counter electrode: platinum mesh.
Figure 3.4 Schematic representation of electrochemical functionalization of SWNTs.
**Figure 3.5a** SEM image of bare SWNTs. Inset showing the nanotube bridging the gold electrode.

**Figure 3.5b** SEM image of TPP polymer coated SWNTs. Inset showing the nanotube bridging the gold electrode.
Figure 3.5c Raman spectra ($\lambda_{ex} = 532$ nm) of SWNTs and SWNT hybrids showing the D and G bands before (blue; $I_D/I_G = 0.079$), after modification with TPP (black; $I_D/I_G = 0.083$) and polyTPP (red; $I_D/I_G = 0.769$).

Figure 3.5d $I_D - V_D$ curve showing the resistance of SWNTs before (blue; 1 kΩ) and after functionalization with TPP polymer (red; 350 kΩ); poly TPP (inset) magnified $I_D - V_D$ curve of SWNT-poly(TPP) hybrid.
Figure 3.5e FET curves showing change in $I_{on}/I_{off}$ ratio before (blue; $I_{on}/I_{off} = 1.5$) and after (red; $I_{on}/I_{off} = 4.7$) electrochemical functionalization of SWNTs with TPP.

Figure 3.5f ATR-IR spectra of SWNT (blue / I), SWNT-TPP (black / II) and SWNT-poly(TPP) (red / III).
Figure 3.6a The real-time nanosensor relative responses ($\Delta R / R_0$) of the SWNT-poly(TPP) devices prepared at various charge densities from 7.68 to 27.51 mC/cm$^2$ to acetone vapor exposure at a concentration of 12.5, 25 and 50% of saturated vapor.

Figure 3.6b Sensor relative responses ($\Delta R/R_0$) to acetone vapor exposure at 12.5 (black square), 25 (red circle), and 50% (blue triangle) of saturated vapor versus charge density applied during constant potential electropolymerization (at 2 V) of tetraphenyl porphyrin (TPP) on SWNTs network. An optimum sensor response is seen at 19.65 mC/cm$^2$ charge density.
Figure 3.7a Transfer characteristic ($I_D-V_G$ curves at $V_{DS} = 1\text{V}$) of SWNTs-poly(TPP) (prepared at 23.59 mC/cm$^2$) in presence of air and saturated vapor of acetone.

Figure 3.7b Normalized transfer characteristic ($I_{D,\text{normalized}}-V_G$ curves at $V_{DS} = 1\text{V}$) of SWNTs-poly(TPP) devices prepared at various charge densities from 7.86 to 27.51 mC/cm$^2$ in presence of saturated vapor of acetone

$$I_{D,\text{normalized}} = \frac{I_{D,\text{acetone (saturated vapor)}}}{I_{D,\text{air (at } V_G = -40\text{) }}}.$$
Figure 3.7c Normalized change in carrier concentration ($-\Delta n/n_o$) versus charge density applied during electropolymerization. $-\Delta n/n_o = [(n_{saturated \ vapor \ of \ acetone} - n_o)/n_o]$, where $n_o$ is the carrier concentration of the device in air.

Figure 3.7d Normalized change in mobility ($\Delta \mu/\mu_o$) versus charge density applied during electropolymerization. $\Delta \mu/\mu_o = [\mu_{saturated \ vapor \ of \ acetone} - \mu_o]/\mu_o$, where $\mu_o$ is the mobility of the device in air.
Figure 3.8a AFM images of before and after electropolymerization of TPP (at 19.65 mC/cm$^2$ charge density) on SWNTs with line scan.

Figure 3.8b Height distribution of bare and TPP polymer coated SWNTs (fabricated at 19.65 mC/cm$^2$ charge density) versus diameter of the SWNTs obtained from AFM analysis. Gaussian fitting of the height distribution provides the average diameter of the nanotubes. Average diameter of the SWNTs increases from $\sim$3 nm to $\sim$7 nm after electropolymerization.
Figure 3.9a Real-time sensor relative responses ($\Delta R / R_0$) to acetone vapor exposure at concentrations varying from 12.5 to 50 % of saturation.

Figure 3.9b Relative responses ($\Delta R / R_0$) of bare SWNTs (black square), SWNT-TPP (red circle) and SWNT-poly(TPP) (blue triangle) versus acetone vapor concentration. The sensors responses increase with the concentrations of acetone. Approximately a four-fold increase in relative response is seen for TPP polymer coated SWNT devices with respect to others.
Figure 3.10a The real-time relative responses ($\Delta R / R_o$) of SWNT-poly( TPP) hybrid (fabricated at optimum charge density) to acetone vapor exposure at concentrations varying from 50 to 2000 ppm as indicated.

Figure 3.10b Calibration curve of SWNT-poly( TPP) sensor towards acetone vapor. Sensitivity can be computed from Langmuir-like isotherm fit curve indicated by (i). The limit of detection (LOD) can be computed from the linear fit line at the lower concentration range indicated by (ii). Response from higher concentration range follows a linear relationship indicated by line (iii).
Figure 3.11a The real-time nanosensor relative responses ($\Delta R / R_0$) of the SWNT-poly(TPP) device (prepared at 19.65 mC/cm$^2$ charge density) to 50% saturated acetone vapor exposure at various days varying from 0 to 180 days.

Figure 3.11b Sensor relative response ($\Delta R / R_0$) of SWNT-poly(TPP) hybrid (fabricated at optimized charge density) at 50% saturated vapor of acetone versus numbers of days. After initial decrease in sensor response, no change is seen after 60 days.
Figure 3.12a The real-time responses ($\Delta R / R_0$) of bare SWNTs and SWNT-poly(TPP) device to benzene vapor exposure at concentrations varying from 1.25 to 15 ppm.

Figure 3.12b SWNT-poly(TPP) sensors relative responses ($\Delta R / R_0$) versus BTEX vapor concentration. Each data point is an average of the measurements from 4 independent sensors prepared at different time and error bars represents ±1 standard deviation.
Figure 3.12c Calibration curve of SWNT-poly(TPP) device for benzene vapors at lower concentration showing a linear relationship.
Figure 3.13 Transfer characteristic ($I_D - V_G$ curves at $V_D = 1$ V) of SWNTs-poly(PPP) device in presence of air and 15 ppm of BTEX vapors.
CHAPTER 4

Sub-ppm Level Detection and Identification of BTEX Compounds
Using Single-Walled Carbon Nanotube-poly(Metalloporphyrin) Sensor Arrays

Abstract

In this chapter, we have demonstrated the synthesis, characterization and fabrication of electrochemically functionalized SWNT-metalloporphyrin hybrid sensor arrays and evaluated its potential for detection and identification of benzene, toluene, ethylbenzene and xylenes vapors. SWNTs networks were functionalized with poly(tetraphenyl prophyrrins) with Iron, Copper and Ruthenium metal centers by electrochemical polymerization. All the hybrids showed a significant response towards benzene, toluene, ethylbenzene and xylenes starting from 1.25 ppm of analyte exposure with a sub ppm limit of detection. The sensor sensitivity was also observed to increase with increased electronegativity of the metal in the hybrid. The principle component analysis confirmed the presence of a definite pattern in sensor response for different hybrid materials and could efficiently discriminate the analytes from one another. Excellent sensitivity and the discriminating capability of the hybrid sensors open up the possibilities for further development of highly dense sensor arrays for E-nose applications.
### 4.1 Introduction:

Detection and quantification of volatile organic compounds (VOCs) are of importance for many applications, including air quality monitoring in both indoor and outdoor environment, occupation safety and toxicology studies. Among these VOCs, benzene, toluene, ethylbenzene and xylenes, commonly known as BTEX compounds, are of particular interest due to their adversary effects towards human health. The toxicity level of benzene is highest within BTEX and it is carcinogenic. Other BTEX compounds are less toxic than benzene. However, numerous health issues may arise including, respiratory problem, eye and skin irritation, and abnormal development of the fetus in pregnant women leading to the birth defect if exposed for long term, even if at a very low concentration. Automobile exhaust and chemical process industries are the major sources of these compounds as a pollutant in the environment. To ensure human health safety, Occupational Safety and Health Administration (OSHA) has fixed the permissible exposure limit (PEL) to 1, 200,100 and 100 ppm for benzene, toluene, ethylbenzene and xylenes, respectively.

Despite of the recent developments, the task of analysing multiple chemicals in a complex environment having thousands of interfering chemicals using an inexpensive device in real time remains a difficult challenge. In sensor technology, a common strategy of specific binding between a sensory element and a target molecule is commonly followed to develop a sensitive and target selective sensor. However, the slow recovery due to the strong binding between the sensor probe and the analyte makes it difficult for real time/dynamic monitoring application. Further, it is very difficult to
employ this strategy for aromatic hydrocarbon detection due to their weak interaction with the probe molecule. Commonly used detection strategies for these compounds are separation-based techniques, including gas chromatography/mass chromatography (GC/MS). Conventional GC/MS equipment is slow, expensive and bulky. Portable GS devices using various detectors have been developed, but their limited sensitivity and selectivity, high cost and relatively bigger equipment size for many applications are the major drawbacks for real world applications. An alternative strategy for VOCs detection could be based on pattern recognition using an array of sensing element. In array-based sensor, selecting the right sensory element could enhance the device performance and selectivity issue will be taken care of by the pattern recognition. In Chapter 3, we showed that the electrochemical functionalization of SWNTs networks with porphyrin can enhance sensitivity of the sensors towards VOCs and in Chapter 2, it was shown that an analyte can be identified as well as quantified by using an array of sensor which could be developed through surface modification of SWNTs with various porphyrins and metalloporphyrins.

In this chapter, we propose an electrochemical method for SWNT-metalloporphyrins hybrid fabrication through covalent modification of SWNTs, which eventually ends up with the surface of SWNTs being coated with the metalloporphyrin polymer and yields a SWNTs-poly(metalloporphyrin) hybrid. Electrochemical method facilitates a better control over the fabrication process and provides a full coverage of the SWNTs surface. The full surface coverage and the presence of more amount of porphyrin as compared to noncovalently functionalized SWNTs contributed toward the
performance enhancement of the sensor. Tetraphenylporphyrin having various metals (Fe, Cu and Ru) were used for this work.

To estimate the potential of the SWNT-based hybrid nanostructures fabricated through electropolymerization of metalloporphyrin (MTPP) on SWNTs network for the development of chemiresistor sensor, sensing performance was evaluated by exposing them to a concentration of 1.25 -15 ppm of BTEX vapors. A significant sensing response at the lowest test-concentration of all test-analytes and a sub-ppm limit of detection (LOD) were observed for all hybrid devices. PCA results suggest that the sensor arrays, which were built using the test hybrid, can successfully differentiate the analytes from each other. FET measurements at various BTEX concentrations indicate that the sensing mechanism is governed by charge transfer or dominated by electrostatic gating effect.

4.2 Experimental Details:

4.2.1 Nanosensor Fabrication:

Carboxylated SWNTs [P3 SWNT-COOH, 80-90% purity from Carbon Solution Inc. (Riverside, CA)] were dispersed in N,N-dimethylformamide (DMF) (Sigma Aldrich, Spectral grade) by ultrasonication for 90 minutes. The solution was then centrifuged at 31000g to separate the bundled SWNTs from the solution. The supernatant of the centrifuged solution was taken out carefully and used for device fabrication.

Sensor electrodes were micro-fabricated on a highly boron-doped silicon wafer (p-type) by standard lithographic process. An insulating layer of SiO₂, approximately 300 nm in thickness, was first grown on both sides of the Si substrate by low-pressure
chemical vapor deposition (LPCVD). Then, the interdigitated electrodes (electrode finger L X W: 100 mm X 5 mm, gap between each finger: 3 mm, total number of fingers: 20) were patterned on the SiO$_2$/Si substrate by photolithography using the positive photoresist AZ-5214, followed by the deposition of a 20 nm thick Cr layer and a 180 nm thick Au layer by e-beam evaporation. Finally, lift-off process was performed to define the electrodes by removing the photoresist.

To bridge the gap between the Au-pad of electrodes, SWNTs were aligned across the electrodes using dielectrophoresis (DEP) technique by placing 0.2 µl of SWNT-suspended solution on the top of the electrode gap while applying 3 V$_{p-p}$ at a frequency of 4 MHz by a function generator (Wavetek, San Diego, CA). To minimize the contact resistance between the Au-pad and the SWNTs, the electrode was annealed at 300 °C for 90 minutes in a reducing environment (5% H$_2$ in N$_2$), which removes any residual DMF between the Au-pad and the SWNTs.

4.2.2 Electrochemical Functionalization:

The surface functionalization of SWNTs was performed through electropolymerization of metallocorphyrins on the surface of SWNTs at room temperature by using a three-electrode electrochemical cell configuration. The SWNTs network served as a working electrode (WE). One of the gold electrodes, without the SWNT network worked as a counter electrode (CE) and a silver wire in AgNO$_3$ (Ag / AgNO$_3$ (0.02 M) in acetonitrile) served as a reference electrode (RE). Electropolymerization was done at a constant potential of +2V versus Ag/AgNO$_3$, in a deoxygenated electrolytic solution of 0.2 M tetrabutylammonium perchlorate (TBAP)
and 2 mM of metalloporphyrin in dichloromethane (CH$_2$Cl$_2$). During polymerization, the amount of total charge was kept constant and the amount of applied charge was varied to manipulate the polymer thickness. After polymerization, the device was rinsed several times with CH$_2$Cl$_2$ followed by nanopure water to remove the unbound monomers and salts and finally dried with nitrogen gas.

The electropolymerization was performed in a custom made electrochemical cell, which allowed the electrode-exposed area to the electrolyte to be constant every time. The charge density of electropolymerization was computed based on the gold electrode area exposed to the electrolyte.

4.2.3 Characterizations:

The structural characterization of the hybrid was done using atomic force microscope (AFM) and spectroscopic characterization was done using Raman spectrometer and attenuated total reflectance (ATR)-IR spectrometer. AFM images were taken using a Veeco Innova AFM. Raman spectra were collected in Nicolet Almega XR Dispersive Raman microscope with a 0.7 µm spot size and 532 nm laser excitation, and the ATR-IR spectra were taken using a Thermo Nicolet Nexus 670 FTIR instrument.

Electrical characterization was done using a semiconductor parameter analyzer (HP model no. 4155A) through current-voltage (I-V) and FET measurements. During FET measurements, the aligned SWNTs/SWNTs-poly(metalloporphyrin) hybrid acted as the channel while the gold electrodes served as the source and the drain. Highly doped Si substrate acted as a back-gate. A dielectric layer of 300 nm thick SiO$_2$ was used to separate the back gate from the source-drain. The fixed potential of 1 V was applied
between the source and the drain while the gate voltage was swept from -40 to 40 V. The source-drain current (I_D) was recorded at room temperature as a function of the applied gate voltage (V_G).

4.2.4 Gas sensing studies:

A custom made sensing system was designed to perform the sensing experiment using Keithley 2636 dual-channel system as a source-meter and a multiplexer to connect all of the sensors with the source meter for simultaneous measurement. During measurement, a bias potential of 0.5 V was applied across each sensor, and the resistance of the sensor was recorded with respect to time. An in-house developed LabView program was used to control the entire process and also to record the data generated during the sensing experiment. The sensor was covered with a 15 (Is this 13 or 15??) cc sealed glass dome with a gas inlet and outlet. Dry air (purity: 99.998%, Air gas Inc. Riverside, CA, USA) was used as carrier gas and saturated VOCs vapor was generated by passing dry air though a bubbler filled with liquid VOCs. Different concentrations of the analyte vapor were obtained by mixing the analyte vapor stream and the dry air. A series of mass flow controllers (Alicate Scientific Inc, Tucson, AZ) were used to control the gas flow rate and to get the desired analyte concentration. In all the experiments, sensors were first exposed to dry air to achieve the baseline, then to a desired concentration of analyte vapor concentration, and then back to air, which completed one cycle.
4.3 Results and Discussion:

To make SWNT-poly(metalloporphyrin) hybrids, electropolymerization was performed at a fixed potential of +2 V vs Ag/AgNO₃. The working potential was chosen based on our previous work reported in Chapter 3 and it was also close to the earlier reported value. Three different types of metalloporphyrin were used for this work, i.e., ruthenium tetraphenylporphyrin (RuTPP), copper tetraphenylporphyrin (CuTPP) and iron tetraphenylporphyrin (FeTPP). As mentioned previously (Chapter 3), the monomer looses three electrons, one at a time, during oxidative electropolymerization process and is oxidized into its radical-cation form \( [M\text{-TPP}^+] \), dication form \( [M\text{-TPP}^{2+}] \) and radical-cation form \( [(M\text{-TPP}^{2+})^+] \), respectively. Then, the radical-cation \( [(M\text{-TPP}^{2+})^+] \) first binds covalently at the sidewall of the SWNT through C-C bond formation (SWNT-aryl bond) and further reacts with another radical-cation \( [(M\text{-TPP}^{2+})^+] \) through aryl-aryl bonding to form metalloporphyrin polymer, which results in SWNT surface coating.

The formation of the SWNT-poly(iron tetraphenylporphyrin) hybrid (SWNT-poly(FeTPP)) was verified by spectroscopy (Raman and (ATR)-IR), microscopy (AFM) and electrical \( (I_D-V_D\text{ and } I_D-V_G) \) studies of a FeTPP-functionalized device. In the Raman spectra, the characteristic peaks of semiconducting SWNTs, i.e. the \( G^- \) band at ~1565 cm⁻¹ and \( G^+ \) band at 1590 cm⁻¹ along with a D band at ~1340 cm⁻¹ and 2D band at ~2675 cm⁻¹ were evident (figure 4.1a). The appearance of a small D band for bare SWNTs was observed due to the presence of carboxyl group at the end terminal of the nanotubes. A significant increase in \( I_D/I_G \) ratio after FeTPP electropolymerization was observed which is attributed towards the increase in defect sites due to the conversion of sp2 carbon
center into sp3 carbon center in the SWNTs lattice via C-C bond formation between SWNT and phenyl group of the metalloporphyrin. A decrease in $I_{2D}/I_G$ ratio was also noticed as expected. Further, a significant increase in resistance (about a few hundred fold) (figure 4.1.b) along with an increase in $I_{on}/I_{off}$ ratio and a decrease in transconductance ($dI_D/dV_G$) (figure 4.1c) indicate an increase in defect site in the SWNTs due to the delocalization of sp$^2$ carbon center and formation of sp$^3$ carbon center, which are in agreement with the Raman spectra results. In the attenuated total reflectance (ATR)-IR spectrum of SWNT-poly(FeTPP) (Figure 4.1d), the presence of the characteristic bands at about 845 cm$^{-1}$, which ascribe to the out-of-plane CH wagging vibration of the biphenyl group formed due to aryl-aryl coupling, further confirms the formation of FeTPP polymer. The Fe peak in the energy-dispersive X-ray (EDAX) spectrum (Figure 4.2.a) assured the presence of Fe in SWNT-poly(FeTPP) hybrid. Absence of Fe peak in the EDAX spectrum (Figure 4.1b) of the control sample, which was prepared through incubation of SWNTs into FeTPP solution for significant amount of time comparable with the electropolymerization time, further confirmed the presence of Fe in the SWNT-poly(FeTPP) hybrid due to polymerization only.

To find out the optimum for the electropolymerization charge-density, the SWNT-poly(FeTPP) hybrids were fabricated by applying various charge densities and evaluating the device performances on the basis of sensing performance towards various acetone vapor concentrations. An increase in hybrid resistance was observed upon exposure to acetone. Dynamic response of the hybrid prepared at various charge densities was recorded in terms of normalized resistance change $[(\Delta R/R_o \%) = (R-R_o) / R_o \times 100]$;
where \( R \) is the resistance of the hybrid exposed to analyte and \( R_o \) is the initial base line resistance before analyte exposure. The sensing responses of the SWNT-poly(FeTPP) hybrid were computed from the dynamic response data and plotted as normalized resistance change with respect to the charge density applied during electropolymerization in Figure 4.3a. Initially an improvement in sensing response was observed with the increase in charge density as the response reaches its maximum value at 11.76 µC/cm\(^2\). However, a decreasing trend in response was observed with further increase in charge density. A similar characteristic was observed for SWNT-poly(CuTPP) (Figure 4.3b) and SWNT-poly(RuTPP) (Figure 4.3c) hybrids when the sensing response was plotted as a function of charge density. Results indicate that the optimum charge densities for hybrid fabrication are not same for all metalloporphyrins. The optimum charge densities for SWNT-poly(metalloporphyrin) were found to be 11.76 µC/cm\(^2\) for FeTPP and RuTPP and 19.58 µC/cm\(^2\) for CuTPP hybrid.

Structural characterization of the SWNT-poly(FeTPP) hybrid fabricated at optimized charge density was done by AFM analysis. Figure 4.4a shows SWNTs bridging the gap between two gold pads of an electrode. The AFM image (before and after functionalization with FeTPP polymer) along with the line scan confirm an increase of ~8 nm in the diameter of SWNT, after coating (Figure 4.4b).

The sensing performance evaluation of SWNT-poly(M-TPP) devices prepared at optimized charge density was done by exposing them to various concentrations of BTEX vapors ranging from 1.25 to 15 ppm. An increase in the device resistance was observed for all hybrids when exposed to BTEX vapors. Figure 4.5a illustrates a representative
real time sensing response in terms of normalized resistance change with respect to time of SWNT-poly(FeTPP) device towards ethylbenzene, while Figures 4b to 4d present the calibration plots of the three metalloporphyrin-SWNTs hybrid sensors for BTEX vapors. As observed in these figures, the relationship between the response and concentration of BTEX over the investigated concentration range for the SWNT-poly(FeTPP) (Figure 4b) and SWNT-poly(CuTPP) (Figure 4c) hybrid devices is linear whereas it is Langmuir-like for SWNT-poly(RuTPP) device (Figure 4d). The limit of detections (LOD) of BTEX was calculated from the calibration curve of the SWNT-poly(M-TPP) devices considering a signal-to-noise ratio of 3 and is summarized in Table 4.1. In case of SWNT-poly(RuTPP) device, the linear range of the calibration curve at lower concentration was considered while calculating the LODs. Sub ppm level LODs for all the devices were observed for BTEX compounds, which are well below their OSHA PEL (OSHA PEL for benzene, toluene, ethylbenzene and xylenes are 1, 200, 100 and 100 ppm, respectively). It is noteworthy that no response was observed towards BTEX vapors (data not shown) for bare SWNT devices.

From the calibration curves of the hybrids, it’s very difficult to have an idea about the role of various metals that are present at the center of the porphyrin towards sensing performance. To understand the role of the metals towards sensing performance, the sensing results were revisited in a different way and grouped together on the basis of analyte. Figure 4.6a, figure 4.6b, figure 4.6c and figure 4.6d represent the sensing results of the three hybrid devices (SWNT-poly(FeTPP), SWNT-poly(CuTPP) and SWNT-poly(RuTPP)) towards benzene, toluene, ethylbenzene and xylenes, respectively.
Pauling scale, the electronegativity of Fe, Cu and Ru are 1.83, 1.88 and 2.2, respectively. The sensitivity of a hybrid sensor could be influenced by the electronegativity of the metal present in the hybrid. A higher electronegative metal could facilitate better charge transfer with respect to a lower electronegative metal while interacting with an electron donating species like BTEX and thus, sensing response could be enhanced. An increasing trend in sensing response was observed with the increase in electronegativity of the metal present in the porphyrin for benzene as well as other analytes (Figure 4.6). These results suggest that a right metalloporphyrin could be chosen for making a sensitive sensor considering the electronegativity of the metal.

In order to have an understanding about the sensing mechanism, FET measurements were carried out for SWNT-poly(FeTPP) hybrid device upon exposure to dry air or 15 ppm of the BTEX vapor concentration. A decrease in drain-current and the threshold voltage ($V_{TH}$) shift towards the negative direction with respect to air were observed for each case when exposed to BTEX vapor (Figure 4.7). BTEX are electron-donating species, hence on adsorption, these analytes donate electrons to the surface of the p-type SWNT semiconductor resulting in a decrease in carrier (hole) concentration. This causes a negative shift in $V_{TH}$ and a reduction in conductivity of the device. Almost no change in the transconductance (slope of the $I_D-V_G$ curve) was observed for air as well as for BTEX exposure. Thus, the significant change in $V_{TH}$ and almost no change in transconductance indicate that the sensing mechanism is governed by electrostatic gating effect.\textsuperscript{8}
To evaluate the BTEX identification performance of the SWNT-poly(M-TPP) sensor arrays principal component analysis (PCA), an eigenvector-based multivariate analysis technique, was used. PCA reduces the dimensionality of numerical data sets through the maximization of variance of the data set. The data matrix was constructed using peak responses from four sensors of the three kind of hybrid devices (SWNT-poly(FeTPP), SWNT-poly(CuTPP) and SWNT-poly(RuTPP)) as the column and corresponding concentrations of BTEX as the rows. The data matrix had 28 rows and 12 columns. In our case, we observed that almost 99% of the total covariance was taken care off by the first three principal components. The first principal component (PC1) accounted for 80.89%, the second principle component (PC2) accounted for 15.78% and the third principal component (PC3) accounted for 2.54% of the total variance. Visual analysis is possible when the scores of the data points are plotted in the PC space. The score plot of PC1 vs. PC2 (Figure 4.8a) indicates that the analyte vectors are different from each other and the scores of the PC1 components increases with the increase of analyte concentration. Further the score plot of PC2 vs. PC2 (Figure 4.8b) shows that the each analyte vapors clustered together and, these clusters are well separated from each other.

4.4 Conclusions:

In summary, we have fabricated single-walled carbon nanotube-poly(metalloporphyrin) sensor arrays through electrochemical route and evaluated their sensing potential towards BTEX vapors. An optimum charge density was found to get the highest sensitivity of the hybrid. Significant sensing response was observed at the lowest
concentration of BTEX at 1.25 ppm. Results indicated that the sensitivity of the hybrid toward the test analytes increases with the increase in electronegativity of the metal present at the center of the TPP. All hybrid devices showed a sub-ppm level LOD for BTEX vapors. FET analysis at exposure to BTEX vapor revealed that electrostatic gating effects governs the sensing mechanism of the hybrid device. PCA analysis revealed a definite pattern in sensor response for different hybrid materials and could differentiate BTEX vapors from each other. The ability of analyte detection well below OSHA PEL level and the discriminating capability of the hybrid devices along with the availability of various types of synthetic porphyrins open up a possibility to develop a highly sensitive and dense nanosensor array for E-nose applications.
4.5 References:


Table 4.1 Limit of detection (LOD) of the hybrid sensor towards BTEX in ppb.
Figures:

**Figure 4.1a** Raman spectra ($\lambda_{ex} = 532$ nm) of SWNTs showing the D and G bands before (red) and after electrochemical functionalization with FeTPP (blue).

**Figure 4.1b** $I_D - V_D$ curve showing the resistance of SWNTs before (red) and after functionalization with FeTPP polymer (blue); (inset) magnified $I_D - V_D$ curve of SWNT-poly(FeTPP) hybrid.
Figure 4.1c FET curves showing change in $I_{on}/I_{off}$ ratio before (red; $I_{on}/I_{off} = \sim 2.8$) and after (blue; $I_{on}/I_{off} = \sim 7$) electrochemical functionalization of SWNTs with FeTPP.

Figure 4.1d ATR-IR spectra of SWNT (red / I), SWNT-FeTPP (black / II) and SWNT-poly(FeTPP) (blue / III).
Figure 4.2a Energy-dispersive X-ray (EDAX) spectrum of SWNT-poly(FeTPP) device; (inset) magnified image of the same.

Figure 4.2b Energy-dispersive X-ray (EDAX) spectrum of the control device (device prepared by incubating the SWNTs in FeTPP solution for 1 minute, followed by three times washing with DMF and water, respectively); (inset) magnified image of the same.
Figure 4.3 Sensor relative responses ($\Delta R/R_0$) to acetone vapor exposure at 12.5 (green, up-triangle), 25 (red, rhombus), and 50% (blue, down-triangle) of saturated vapor versus charge density applied during constant potential electropolymerization (at 2 V) of (a) FeTPP (b) CuTPP and (c) RuTPP on SWNTs network.
**Figure 4.4a** AFM image showing the Au pads bridging by the SWNTs.

**Figure 4.4b** AFM image and corresponding line analysis of bare SWNTs and SWNT-poly(FeTPP) hybrid.
Figure 4.5 (a) Real time sensing response of SWNT-poly(FeTPP) device towards ethylbenzene vapors. Calibration curves of (b) SWNT-poly(FeTPP), (c) SWNT-poly(CuTPP) and (d) SWNT-poly(RuTPP) devices towards benzene (green, square), toluene (red, circle), ethylbenzene (blue, star) and xylenes (magenta, triangle) vapors, respectively.
Figure 4.6 Calibration curves of SWNT-poly(FeTPP) (blue, star), SWNT-poly(CuTPP) (red, circle) and SWNT-poly(RuTPP) (green, square) devices towards (a) benzene, (b) toluene, (c) ethylbenzene and (d) xylenes vapors.
Figure 4.7 Transfer characteristics ($I_D - V_G$ curves at $V_D = 1$ V) of SWNTs-poly(FeTPP) device in presence of air and 15 ppm of BTEX vapors.
Figure 4.8a PCA plot (PC1 vs PC2) of scores using three sensors (SWNT-poly(FeTPP), SWNT-poly(CuTPP) and SWNT-poly(RuTPP) for BTEX compounds.

Figure 4.8b PCA plot (PC2 vs PC3) of scores using three sensors (SWNT-poly(FeTPP), SWNT-poly(CuTPP) and SWNT-poly(RuTPP) showing well-separated clusters for BTEX compounds.
CHAPTER 5

Single-walled Carbon Nanotube-Calixarene Chemiresistive sensor for Volatile Organic Compounds

Abstract

In this chapter, we report a sensitive chemiresistive sensor for benzene, toluene, ethylbenzene and xylenes detection at ambient condition using single-walled carbon nanotube-calixarene hybrid network. The sensor was fabricated by the combination of dielectrophoretic alignment of the nanotube on a prefabricated microelectrode and solvent casting technique. These sensors showed an increase in resistance upon exposure to successive increments of the analyte concentration from 50 to 250 ppm with a limit of detection, except for benzene, well below the OSHA PEL. Field-effect transistor studies indicate the sensing mechanism is dominated by electrostatic gating effect.
5.1 Introduction:

Calixarenes are organic, macro-cyclic compounds having interesting optical and tunable chemical properties as well as good chemical stability.\(^1\) Its ability to interact with the analyte molecule through weak van der Wall forces, and the measurable property change upon calixarene analyte binding makes calixarene an attractive class of sensing material.\(^2\) Further, its bowl like structure with a cavity at the center, having a hydrophobic pendent and ability to adapt to a change from close to planar conformation upon interaction with the analyte make it more specific towards the development of volatile organic compounds (VOCs) sensor. Calixarene-analyte interaction could be manipulated by choosing a calixarene having different cavity size or end-terminal functional groups. A wide variety of calixarenes having different functional groups and different cavity sizes depending on the number of benzene ring is commercially available. There are reports on calixarene-based sensors based on optical\(^3\) and mass transduction.\(^4\) The potential of calixarene as functional material has also been demonstrated, where an organic thin film based field-effect transistor (OTFT) was modified with calixarene to improve sensor sensitivity.\(^5\) The OTFT fabrication require multiple thermal evaporation process to grow the organic semiconductor thin-film as well as to functionalized the semiconductor with calixarene. They also require a high bias-potential \((V_G @ -60 \text{ V})\) and high source-drain potential \((V_{DS} = -60 \text{ V})\) to operate. In some cases, limited sensitivity and large volume of the sensor assembly are also restricting their use for practical and mobile applications. In this context, a chemiresistive sensor based on conductivity change could be the simplest possible transduction mechanism, which requires simple
technology for electronic applications. However, very low electrical conductivity of calixarene is the major impediment to develop a chemiresistive sensor exclusively based on calixarene.\textsuperscript{6}

On the other hand, single-walled carbon nanotubes (SWNTs) have gained attention in sensing applications owing to their superior electrical properties and chemical stability at ambient condition, compared to other conventional semiconducting materials.\textsuperscript{7} In particular, the property of conductance change upon absorption of analyte gas molecules makes SWNTs a promising material for sensor development.\textsuperscript{8} Its high electrical mobility also enables the development of low-power microelectronics and one-dimensional geometry makes it possible to develop a high-density nanosensor array within a limited space. However, the lack of sensor performance in terms of sensitivity limits the use of SWNTs as an individual sensor.\textsuperscript{9} This issue could be overcome through the surface modification of SWNTs with suitable recognition element.\textsuperscript{10} There are reports on sensor performance improvement towards various analytes upon surface modification of SWNTs with polymers,\textsuperscript{9} metals\textsuperscript{11} and metal oxides\textsuperscript{12}. This surface modification strategy paves the way to the possible development of SWNT-calixarene hybrid sensor exploiting the binding ability of calixarene with the analyte gas molecule that facilitates the improvement of sensing performance and the excellent mobility of the SWNTs, which enables development of a low power chemiresistive sensor by improving the hybrid device conductance.

In this work, we report the fabrication of SWNT-calixarene based chemiresistive hybrid nanosensor through dielectrophoretic alignment of SWNTs on a prefabricated
microelectrode by functionalization of SWNTs with calixarene by solvent casting and also the performance evaluation towards VOCs. Among the VOCs, we chose benzene, toluene, ethylbenzene and xylenes (commonly known as BTEX) for our experiment, as they are toxic and known to be carcinogenic. Automobile exhausts gas is the most common source of BTEX in the atmospheric air. As per Occupational Safety and Health Administration (OSHA), these chemicals are harmful to human health and long-term exposure over a permissible exposure limits (PEL) level of 1, 200, 100 and 100 ppm, respectively may cause respiratory problem and/or cancer. Fabricated hybrid sensor showed promising response to BTEX down to 50 ppm at room temperature, which, except for benzene, is well below the PEL level.

5.2. Experimental Details:

The calixarene used here is derived from four resorcinol aromatic rings and is referred to as calix-4-resorcarene. The molecular structure is shown in Figure 5.1.

SWNTs were aligned in the gap between a pair of Au electrodes using dielectrophoresis following the protocol described in Chapter 3. In this work, interdigitated electrodes were used which are same as the electrodes mentioned in Chapter 3. The hybrid fabrication was completed through π-π interaction between the SWNTs and calixarene by incubating the SWNTs with calixarene solution prepared in DMF, followed by washing several times with DMF and water to remove unbound calixarene molecules. The unbound calixarene molecules, which are not connected to the nanotube will also interact with the analyte molecule during analyte exposure without
contributing any property change in the device, or may hinder the charge transfer process to SWNTs causing interference to the device performance.

The nanostructure characterization was done using scanning electron microscope (SEM), Raman spectrometer and attenuated total reflectance (ATR)-IR spectrometer. SEM images were obtained using Zeiss Leo SUPRA 55 with beam energy of 20 kV. AFM images were taken using a Veeco Innova AFM. Raman spectra were collected in Nicolet Almega XR Dispersive Raman microscope with a 0.7 µm spot size and 532 nm laser excitation. The ATR-IR spectra were taken using a Thermo Nicolet Nexus 670 FTIR instrument equipped with an ATR sampling accessory.

FET measurements were also performed by using a semiconductor parameter analyzer (HP model no. 4155A). During FET measurements, the gold electrodes served as the drain and the source while the aligned SWNTs-calixarene hybrid acted as the channel. The back gate potential was applied through the highly doped Si substrate. A dielectric layer of 300 nm thick SiO₂ was used to separate the back gate from the source-drain. The fixed potential of 1 V was applied between the source and the drain while the gate voltage was swept from -40 to 40 V. The source-drain current (I_D) was recorded at room temperature as a function of the applied gate voltage (V_G).

5.3 Results and Discussion:

Scanning electron microscopy (SEM) image of the assembled devices showed that there were multiple SWNTs aligned in an ordered manner between the gold
electrodes (Figure 5.2a, inset)). An increase in device resistance was observed after functionalization of SWNTs with the calixarene (Figure 5.2a). The identical I_D-V_G curves (Figure 5.2b) of the bare and functionalized SWNTs having almost no change in I_on/I_off ratio and transconductance (dI_D/dV_G) indicates that the hybrid retains its original semiconducting properties except a slight loss in device conductance. Again, in the Raman spectroscopy, an unchanged appearance of radial breathing mode (RBM) around 100-300 cm\(^{-1}\) along with a D-band at \(~1340\) cm\(^{-1}\), a G\(^{-}\)-band at \(~1570\) cm\(^{-1}\), a G\(^{+}\)-band at \(~1590\) cm\(^{-1}\) and 2D-band at \(~2675\) cm\(^{-1}\) without having any significant alteration of I_D/I_G ratio after functionalization indicates a noncovalent modification of SWNTs without any change in electronic properties (Figure 5.2c).\(^{13}\) Further, in the attenuated total reflectance (ATR)-infrared (IR) spectroscopy, the presence of reflectance bands within the range of 1000 to 1165 and 1580 to 1600 cm\(^{-1}\) that ascribe to the C-H bending and C=C stretching along with a broad spectra at 3290 cm\(^{-1}\), which ascribes to the O-H stretching of the aromatic component for SWNT-calixarene, confirmed the successful hybrid formation (Figure 5.2.d).

To evaluate the performance of the hybrid device, it was connected to a chip holder by wire bonding and placed in a glass chamber with inlet and outlet ports. Dry air or air/analyte mixture at a total flow rate of 200 sccm was flown into the glass chamber using mass flow controllers (MFCs). During the sensing experiment, 0.5 V bias potential was applied across the device and the change in resistance upon exposure to the analyte gas was continuously determined using a dual channel Keithley Source Meter (Model 2363A). A custom made LabVIEW computer program was used to control the mass flow
meters and to record the resistance of the device. The sensing experiment was started by first purging the glass chamber with dry air for 200 min to stabilize the resistance of the sensor, followed by increasing analyte concentration in air every 15 min with an interval of 20 min recovery in air between two successive analyte exposures. The real time sensing response in terms normalized change in resistance $[(R/R_0)/R_0]$, where $R$ and $R_0$ are the resistances in ethylbenzene vapor and air, respectively] as a function of time was recorded and showed in Figure 5.3a. An immediate increase in device resistance in significant magnitude was noticed when exposed to ethylbenzene as well as to other analyte vapors. This is attributed to ethylbenzene being an electron donor, which would reduce the charge carrier (hole) density by injecting the electron to the surface of the SWNTs when absorbed, thereby resulting in an increase in device resistance. However, no response towards ethylbenzene was observed for bare SWNT devices. The calibration curves of BTEX, shown in Figure 5.3b, indicate a nonlinear relationship and can be best represented by a Langmuir-like absorption isotherm, where the relationship between the normalized resistance change $(\Delta R / R_0)$ and the concentration $(c)$ is governed by the equation

$$\frac{\Delta R}{R_0} = \left(\frac{\Delta R}{R_0}\right)_{\text{max}} \cdot \frac{c}{k + c},$$

where $(\Delta R / R_0)_{\text{max}}$ is the maximum change in normalized resistance occurring in the saturation regime, and $k$ is the affinity constant. The limit of detection (LOD) was calculated from the liner range of the calibration curve in the lower concentration range, considering a signal-to-noise ratio of 3. The sensitivity $(S)$ of the sensor was
computed by taking the derivative of the equation with respect to analyte concentration at low concentration, i.e., considering $k + c = k$. The constants $(\Delta R / R_0)_{max}$ and $k$ values along with sensitivity and LOD are depicted in Table 5.1. It is evident that SWNT-calixarene hybrid provides a significant sensing response at a concentration of 50 ppm for all analytes (Figure 5.3b) and calculated LOD well below their PEL level except benzene (Table 5.1).

In order to have an understanding about the sensing mechanism, FET measurements were carried out for SWNT-calixarene hybrid upon exposure to dry air or 200 ppm of the analyte concentration. A negative shift of threshold voltage ($V_{TH}$) and an insignificant change in transconductance ($dI_D/dV_G$) with respect to air were observed when exposed to analyte vapors (Figure 5.4). BTEX are electron-donating species, hence on absorption these analytes donate electron to the surface of the p-type SWNT device resulting in a decrease in carrier (hole) concentration, thereby causing a negative shift in $V_{TH}$ and reduction in conductivity of the device. Thus, the significant change in $V_{TH}$ and insignificant change $dI_D/dV_G$ indicate that the sensing mechanism is governed by electrostatic gating effect.\textsuperscript{15} It is noteworthy that the change in $V_{TH}$ upon analyte exposure is in agreement with the sensing result as shown in Figure 5.3b.

\textbf{5.4 Conclusions:}

In summary, the SWNT-calixarene hybrid chemiresistive sensor for BTEX at ambient temperature has been described. A simple dielectrophoretic alignment and solvent casting techniques were used to fabricate the sensor. The sensor was able to
detect BTEX vapor down to 50 ppm, which, except for benzene, is well below the OSHA PEL levels. The FET analyses revealed that the sensing mechanism of the SWNT-calixarene device is governed by the electrostatic gating effect. The experiments showed that the sensor is highly sensitive towards all BTEX vapors.
5.5 References:


Table:  

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<th>Sensitivity / ppm$^{-1}$</th>
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*Table 5.1* Room temperature values of the constants $[\Delta R/R_0]_{\text{max}}$ and $k$, sensitivity and LOD of the SWNT-calixarene hybrid for BTEX.
Figures:

Figure 5.1 Molecular structure of calix-4-resorcarene
Figure 5.2 (a) Two terminal source-drain current-voltage ($I_D$-$V_D$) characteristic curves, (inset) SEM image of the aligned SWNTs bridging the source-drain Au electrodes after ac dielectrophoresis. (b) Transfer characteristic ($I_D$-$V_G$ curves in air at $V_D = 1$ V), (c) Raman spectra ($\lambda_{ex} = 532$ nm) and (d) ATR-IR spectra of bare and calixarene functionalized SWNTs.
Figure 5.3 (a) The real-time nanosensor relative responses ($\Delta R / R_0$) to ethylbenzene vapor exposure at concentrations varying from 50 to 250 ppm. (b) Sensors relative responses ($\Delta R / R_0$) versus BTEX vapor concentration.
Figure 5.4 Transfer characteristic ($I_D - V_G$ curves at $V_D = 1$ V) of SWNTs-calixarene hybrid in presence of air and 200 ppm of BTEX vapors.
CHAPTER 6

Label-free chemiresistive biosensor for mercury (II) based on single-walled carbon nanotubes and structure-switching DNA

Abstract

In this work, we present a sensitive, selective and facile label-free DNA functionalized single-walled carbon nanotube-based (SWNTs) chemiresistive biosensor for the detection of Hg$^{2+}$. SWNTs were functionalized with Hg$^{2+}$ binding 15-bases long polyT oligonucleotide through covalent attachment using a bilinker molecule. The polyT was further hybridized with polyA to form a polyT:polyA duplex. When exposed to Hg$^{2+}$ the polyT-polyA duplex was dehybridized combined with switching of polyT structure, leading to change in resistance/conductance of the SWNT chemiresistor device. The device provided a significant response within 100 to 1000 nM of Hg$^{2+}$ concentration with a $6.72 \times 10^{-3}$ / nM sensitivity.
6.1 Introduction:

Mercury (Hg) is a worldwide concern in aquatic environments due to its toxicity and biomagnification in food webs. Elevated exposure to mercury can affect the cardiovascular system, gastro-intestinal system, liver, kidneys and neurological system of the human body.¹ Industrial wastewater from chlor-alkali and mineral industries, burning of fossil fuels, and incineration of municipal solid waste are the major sources of mercury contamination in the environment. The total global mercury emission from all sources has been estimated at 7500 tons per year.² The United States Environmental Protection agency (EPA) has mandated a drinking water upper limit of 2 ppb (10 nM) for mercury (II) ion concentration.³

Protein based Hg²⁺ biosensor using electrochemical⁴,⁵ and optical⁶ techniques have been demonstrated. However, poor stability of proteins at ambient condition restricts its use for real application. These stability issues could be overcome by using DNA molecules that have excellent stability at ambient condition and do not require stringent storage conditions. Highly sensitive and selective detection of Hg²⁺ ion based on thymine-Hg²⁺-thymine (T-Hg²⁺-T) structure-switching DNA using UV absorption, fluorescence, surface-enhanced Raman spectroscopy, resonance scattering and electrochemical methods have been demonstrated.⁷⁻¹² However, these approaches require complex, labour-intensive labelling and/or sophisticated instruments.¹³

Single-walled carbon nanotubes (SWNTs) have been extensively studied as a transducer element in biosensors for their high surface to volume ratio, which results in
the surface phenomena predomination over the chemistry and physics that happen in the bulk. The extreme sensitivity towards resistance/conductance changes in SWNTs due to the surface absorption/perturbation of analyte molecule makes it a potential material for label-free biosensor development.\textsuperscript{14, 15} Further, the high electrical mobility of SWNTs enables to develop low power microelectronics and the one-dimensional (1-D) nanostructure of SWNTs facilitates development of high-density sensor arrays within a limited space. In this work, we propose a label-free, chemiresistive biosensor for Hg\textsuperscript{2+} ion detection based on polyT-polyA duplex functionalized SWNT, which upon exposure to Hg\textsuperscript{2+} results in the dehybridization of polyT-polyA duplex and switching of polyT structure, leading to change in resistance/conductance of the SWNT chemiresistor device.

6.2 Experimental Details:

Electrode fabrication and SWNT alignment processes have discussed in detail in chapter 2. In short, by placing drop of SWNTs suspension between the gaps of the gold electrodes, followed by using DEP technique, aligned the SWNTs between the Au electrodes. Further, the SWNTs were functionalized noncovalently and covalently with polyT.

6.2.1 Non-covalent functionalization of SWNTs with PolyT (Scheme I):

Aligned SWNTs network chemiresistor was incubated with 100 nM of oligonucleotide polyT (5’ – TTT TTT TTT TTT TTT -3’) [Integrated DNA Technologies Inc., San Diago, CA, USA] in 10 mM pH 7.2 phosphate buffer (PB) for 2
hours at room temperature followed by thorough washing with nanopure water to remove unbound oligo. Further, the gold pads of the electrode were blocked by 6-mercapto-1-hexanol (MCH). MCH blocking was done by incubating the device with 6 mM of MCH solution for 1 hour at room temperature. A monolayer of MCH was formed on exposed gold pads of the electrode due to the interaction between thiol group and gold, which restricts further interaction/accumulation of Hg$^{2+}$ on the gold surface.

6.2.2 Covalent functionalization of SWNTs with amino-labeled PolyT followed by hybridization with polyA (Scheme II):

First, SWNTs network chemiresistor was modified with 1-Pyrenebutanoic acid succinimidyl ester (PBASE) by incubating with 6 mM of PBASE in dimethylformamide (DMF) for 1 hour at room temperature followed by washing with DMF three times to remove residual ester. The capture oligonucleotide was then covalently attached to the PBASE-modified SWNTs by incubating overnight at 4 °C with 100 nM amino-labeled polyT (5’-5AmMC6/TTT TTT TTT TTT TTT -3’) [Integrated DNA Technologies Inc., San Diego, CA, USA] in 10 mM pH 7.2 PB through the amide bond between the amine at its 5’ end and N-hydrosuccinimide ester of PBASE washed three time to remove excess oligo. The device was further treated with 0.1 mM ethanolamine (EA) for 30 minutes at room temperature to block excessive reactive groups and incubated with 0.1 % (V/V) Tween 20 in 10 mM pH 7.2 PB for 30 minutes at room temperature to prevent nonspecific binding to SWNTs. The device gold pads were blocked by MCH blocking. Finally, the captured oligo (polyT) was hybridized to polyA (5’ – AAA AAA AAA AAA AAA AAA -3’) [Integrated DNA Technologies Inc., San Diego, CA, USA] by incubating
with 100 nM PolyA in 10 nM pH 7.2 PB solutions for 2 hour at room temperature.

6.2.3. Sensing measurements:

The sensing protocol consisted of 1) monitoring the initial resistance ($R_0$) of the biosensors fabricated using different scheme by measuring the source-drain current (I) as a function of source-drain voltage (V) from -0.5 to +0.5 V using a CHI 1202 (CH Instruments, Austin, TX, USA) electrochemical analyzer and taking the inverse of the slope of the I-V curve from -0.1 V to +0.1 V, 2) incubation for 30 minutes at room temperature with different concentration of Hg$^{2+}$ ion sample in PB, washing three times with PB and water, drying with nitrogen and recording the new resistance.

6.3 Results and Discussion:

Initially we investigated sensing of Hg$^{2+}$ using a polyT-based SWNTs chemiresistive biosensor fabricated through non-covalent functionalization of SWNTs (Scheme I). Figures 6.1 and 6.2, respectively, show the schematic of the fabrication/sensing steps and the current vs. voltage (I-V) responses corresponding to each step. As shown in figure 6.2, the resistance of the SWNTs network increased upon non-covalent immobilization of polyT (5’–TTT TTT TTT TTT TTT -3’) attributed to $\pi$-$\pi$ stacking interaction and the negative charge density provided by the phosphate groups on a polyT-SWNTs hybrid on the p-type SWNTs.$^{17}$ Upon incubation of the final sensor device (after blocking of Hg$^{2+}$ binding with the gold electrodes by a self-assembled
monolayer of 6-mercaptop-1-hexanol (MCH))\textsuperscript{18} with 1 mM Hg\textsuperscript{2+} the device resistance decreased (Figure 6.2). The resistance decrease or conductance increase is a result of removal/release of polyT from the SWNTs surface due to the formation of T-Hg\textsuperscript{2+}-T complex\textsuperscript{19}, a hairpin like structure,\textsuperscript{20} causing a decrease of negative charge on SWNTs and/or thermodynamically favourable reduction of Hg\textsuperscript{2+} on SWNTs\textsuperscript{21} providing a hole carrier injection on SWNTs. While the selectivity of the Scheme I biosensor was very good (Figure 6.3) the sensitivity for Hg\textsuperscript{2+} was low and the relationship of response with the Hg\textsuperscript{2+} concentration was not linear (data not shown).

In order to improve the device performance in terms of sensitivity and selectivity, the fabrication protocol (Scheme II) was modified and the device was fabricated through covalent functionalization of SWNTs with amino-labelled polyT followed by hybridization with polyA (Figure 6.4) to form DNA duplex. Figure 6.5 shows current vs. voltage (I-V) recordings of the fabrication steps and Hg\textsuperscript{2+} sensing: non-covalent functionalization of SWNTs with 1-pyrenebutanoic acid succinimidyl ester (PBASE); covalent attachment of the amino-labelled capture oligonucleotide polyT (5’ -/5AmMC6/TTT TTT TTT TTT TTT -3’) through the amide bond between the amine at 5’ end of the capture oligo and N-hydrosuccinimide ester (NHS) of PBASE; neutralization of unbound NHS with ethanolamine (EA) and blocking of unfunctionalized SWNTs with Tween 20; hybridization of amino-labelled polyT with polyA (5’ –AAA AAA AAA AAA AAA -3’) to form polyT-polyA duplex; MCH blocking of gold pads of the electrode; and sensing of Hg\textsuperscript{2+} ion. An increase in resistance of the SWNTs was
observed after PBASE modification. The resistance of PBASE modified SWNTs remain unchanged after covalent binding of amino-labelled polyT. Further, increase in resistance of the device was noticed for all successive steps of fabrication. The resistance increases were in accordance with the literature and a result of electron donation from these molecules to the nanotubes resulting in charge carrier reduction in SWNTs and/or scattering potential generated by the immobilization of the molecules and thereby decrease in the hole mobility. Upon incubation of the final biosensor with 250 nM Hg$^{2+}$ solution for 30 minutes at room temperature, the source and drain current of the device increased, i.e. the resistance decreased due to the dehybridization of polyT:polyA duplex resulting the formation of T-Hg$^{2+}$-T duplex and the release of polyA from SWNTs surface.

Negative controls, i.e., SWNTs devices functionalized with only the capture oligo and blocked with ethanolamine, Tween 20 and MCH, i.e. without the polyA, showed no response to Hg$^{2+}$ (data not shown). These results confirmed the effectiveness of the proposed sensing modality for Hg$^{2+}$ by a nanostructure-based chemiresistor biosensor.

Figure 6.6 shows the calibration curve, relationship between the SWNTs chemiresistive biosensor response $[(R - R_0) / R_0]$, where R is the resistance after exposure to Hg$^{2+}$ ion and $R_0$ is the resistance of SWNTs after hybridization with polyA and MCH blocking. The resistance was calculated as the inverse of the slope of the I–V curve between -0.1 and +0.1 V (linear range). As shown in the figure 6.6, the sensor response was linear over the Hg$^{2+}$ concentration ranging from 100 nM to
1μM with a 6.72 x 10^{-3} / nM sensitivity. Also more than ten order of enhancement in sensor response was observed as compared to the device fabricated through Scheme I. This enhancement in sensitivity attributed to the extremely high sensitivity of the chemiresistive transduction combined with the displacement principle.\textsuperscript{24}

To examine the selectivity of the biosensors, SWNT devices were incubated with different metal ion solutions of the same concentration. The responses for Hg\textsuperscript{2+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and Mn\textsuperscript{2+} ion were found out to be -18.80±4.8\%, -7.31±2.01\%, -4.28±0.60\%, and -5.13±3.49\%, respectively (Figure 6.7), thus demonstrating that SWNT based chemiresistive biosensors was highly selective for Hg\textsuperscript{2+} ion detection.

6.4 Conclusions:

In conclusion, we have fabricated a SWNTs chemiresitive biosensor for Hg\textsuperscript{2+} ion detection based on structure-switching DNA. This biosensor exhibited good selectivity for Hg\textsuperscript{2+} ion and showed a linear response over the range of concentrations between 100 nM to 1μM Hg\textsuperscript{2+} ion. Furthermore, the SWNTs nano-biosensor is a truly label-free system, requiring the aid of no labels attached to the polyA or the capture oligo.
6.5 References:


Figure 6.1 Schematic illustration of SWNTs chemiresistive label-free biosensor fabrication steps through noncovalent functionalization of SWNTs with polyT (Scheme I).
Figure 6.2 Current versus voltage (I-V) curves of SWNTs chemiresistive label-free biosensor (fabricated via Scheme I) at various stages of fabrication and upon exposure of 1 μM of Hg^{2+}.
Figure 6.3 Responses of SWNTs chemiresistive label-free biosensor (fabricated via Scheme I) to various metal ions. The concentrations of all metal ions were fixed at 1 µM. Data for each metal ion was obtained from four different sensors at different time and error bars represent ±1 standard deviation.
Figure 6.4 Schematic illustration of SWNTs chemiresistive label-free biosensor fabrication steps through covalent functionalization of SWNTs with amino-labeled polyT followed by hybridization with polyA.
Figure 6.5 Current versus voltage (I-V) curves of SWNTs chemiresistive label-free biosensor at different stages of fabrication and upon exposure of 250 nM of Hg$^{2+}$. 

- SWNTs
- PBASE
- Amino-labeled polyT
- EA + Tween 20
- MCH
- PolyA
- 250 nM Hg$^{2+}$
Figure 6.6 SWNTs chemiresistive label-free biosensor calibration for Hg$^{2+}$. Each data point is an average of the measurements from 4 independent sensors prepared at different time and error bars represents ±1 standard deviation.
Figure 6.7 Responses of SWNTs chemiresistive label-free biosensor for different metal ions. The concentrations of the metal ions were 1 µM and incubation period was 30 minutes. Each data point is an average of measurements from four independent sensors at different point of time and the error bars represents ±1 standard deviation.
Detection and quantification of pollutants such as volatile organic compounds (VOCs) in air and heavy metals in water are of prime importance to protect the environment as well as human health. Most VOCs may cause adverse effect on human health when exposed for prolonged times. Some VOCs like benzene and formaldehyde can also cause cancer. On the other hand, heavy metals such as mercury have a deadly effect on human health. Accurate detection of pollutants using conventional analytical methods such as Gas Chromatography, Mass Spectroscopy, and Atomic Absorption Spectroscopy is possible. However, these analytical tools are often bigger in size, expensive and not suitable for in situ applications. Hence nanomaterial based sensors could be a better alternative to provide high sensitivity, reliability and fast response. The smaller size of the nanomaterial-based sensor also facilitates on site and in situ applications.

One-dimensional (1-D) nanostructures have emerged as a potential material in recent time and shown a great promise over thin film based two-dimensional (2-D) structures for sensor applications. In case of 1-D nanomaterial, the surface chemistry dominates the material property change due to their high surface-to-volume ratio and their smaller size provides improvement in sensor sensitivity owing to their comparable
dimension with the Debye length.

Single-walled carbon nanotubes (SWNTs) are a 1-D nanomaterial. They display good mechanical strength, excellent chemical stability and interesting electronic properties. Their one-dimensional (1-D) structure, higher electrical mobility and inertness towards ambient temperature variation facilitate fabrication of low-power, high-density miniaturized sensors for room temperature applications. To improve the sensitivity as well as selectivity, surface modification with metal, metal oxides, conducting polymers, organic macromolecules and biomolecules etc. has been successfully demonstrated. Organic macromolecules such as porphyrins and calixarenes possess interesting structural, optical and chemical properties, and their ability to interact chemically with almost all VOCs make them a potential functional material. Biomolecules, such as polyT (a single stranded DNA), could also be used as potential recognition molecules for mercury ion detection owing to their structural switching capability when in presence of mercury ions. In this dissertation, sensing applications of SWNT based hybrid devices have been demonstrated. The potential of organic macromolecules such as porphyrins and calixarene functionalized hybrid sensors was explored for various VOCs in air medium. Also polyT functionalized SWNT hybrid has been developed for sensitive detection of mercury ion in aquatic environment.

Chapters 2, 3, 4 and 5 describe single-walled carbon nanotube-organic macromolecule based hybrid sensors for detection of VOCs. In Chapter 2, a simple method of SWNT-porphyrin hybrid formation through solvent casting techniques,
characterization and their use towards a wide range of VOCs were described. Differences in sensing performance are observed for porphyrins with different functional groups and with different central metal atoms. Principal component analysis (PCA) analyses confirmed the presence of a definite pattern in response data for different hybrid materials and the ability to differentiate analytes from one another. This discriminating capability of the hybrid devices and availability of a wide range of commercially available synthetic porphyrins open up an opportunity to develop a highly dense nanosensor array for E-nose applications. However, SWNT-porphyrin hybrid provided limited sensor sensitivity and did not comply with the OSHA PEL concentrations. The device sensitivity of SWNT-porphyrin hybrid may be compromised due to the partial surface coverage of the SWNTs with porphyrin when fabricated through solvent casting methods. A full surface coverage of SWNTs is possible through electrochemical functionalization processes, and thus, improvement in device sensitivity could be expected. The fabrication and process optimization of SWNT-poly(porphyrin) hybrid sensor through electrochemical routes were discussed in Chapter 3. Electrochemically modified SWNT hybrid showed superior sensing performance towards VOCs and also provided LODs below their respective OSHA PEL concentrations. Electrochemical methods provide process flexibilities where thickness of the polymer could be manipulated by controlling specific process parameters that facilitate tuning of hybrid material properties. In case of electrochemically functionalized SWNT hybrids, an optimum charge density was found which resulted in the highest sensitivity for the devices. During SWNT-poly(porphyrin) hybrid fabrication, with the increase of polymer
thickness two effects may happen, (1) more number of porphyrin are available to interact with the analytes leading to an enhancement of device sensitivity and (2) device resistivity is increased (as porphyrin conductivity is too low) thereby restricting the charge transfer process resulting in a decreased device sensitivity. Hence, there will be an optimum thickness that will balance between these two effects and provide the best performance of the hybrid device. The SWNT-poly(metalloporphyrin) hybrid fabrication using FeTPP, CuTPP and RuTPP and their demonstration towards benzene, toluene, ethylbenzene and xylenes (commonly known as BTEX compounds) were described in Chapter 4. Metalloporphyrin functionalized SWNT hybrid devices provided a sub-ppm LOD for all BTEX compounds. Further PCA analysis showed a clear discriminating pattern between the BTEX compounds when hybrid sensor arrays were created using polymers of Fe-, Cu- and RuTPP. In case of SWNT-poly(porphyrin) sensor devices, the sensing mechanism was found to be dominated by the electrostatic gating effect. SWNT-calixarene based hybrid fabrication through solvent casting techniques and their use in BTEX detection was demonstrated in Chapter 5. SWNT-calixarene can meet OSHA PEL concentration detection of BTEX compounds except benzene.

In Chapter 6, the functionalized strategy of SWNTs with polyT to make a hybrid device and their application in mercury ion detection was discussed. SWNT-poly hybrid can be attached to the SWNT surface through noncovalent surface absorption. However detachment of the polyT molecule from the SWNTs surface due to structural change upon interaction with the mercury ion results in limited sensitivity. When polyT was covalently attached on the SWNTs surface through a linker molecule and hybridized with
complementary ssDNA (polyA), an improved sensitivity was observed due to the displacement of polyA and structural change of polyT, upon analyte incubation.

Single-walled carbon nanotubes have proven to be ideal starting material in sensing applications. In case of SWNT-poly(metal-TPP) hybrid devices, an increasing trend in sensor response towards BTEX was observed with the increase in electronegativity of the metal. These results give some hints regarding which porphyrin could be selected to develop a hybrid sensor for a target analyte. However, more investigation is needed using a wide variety of porphyrins having different functional groups at the outer periphery of the porphyrin ring or with different metal atoms at the center of the porphyrin ring towards more numbers of VOCs to understand the effect of metals towards sensor response which may provide a generalized rule for porphyrin selection for a target analyte. Further, VOC sensors lack selectivity due to the weak bind of the analyte with the sensory material; hence an array-based sensor is the probable solution to overcome the selectivity issue. However, design and fabrication of a sensor chip having high-density sensor arrays within a limited space are the most important and challenging tasks considering the issues regarding the on-chip electropolymerization and the integration with modern electronics that need to be addressed.
APPENDIX

Photo-induced charge transport in ZnS nanocrystals decorated single walled carbon nanotube field-effect transistor

Abstract

In this chapter, we describe a photoresponse measurement study on a pyrene linked ZnS nanoparticles decorated single walled carbon nanotube (SWNT) field-effect transistor (FET). We observed that the photocurrent response in the system is based on the semiconducting property of the single walled carbon nanotube (SWNT). It was found that both the organic molecule linker, pyrene, together with ZnS nanocrystals contributed to the total photoresponse of the ZnS-pyrene/SWNT hybrid device. We demonstrated by FET characteristic studies that the majority charge carriers in the ZnS-pyrene/SWNT device upon UV illumination are positively charged photo-induced holes near the $p$-type SWNT channel.
A.1 Introduction:

Semiconductor nanocrystals (NCS), also known as quantum dots (QD), because of their size-tuned optical response, and their efficient multiple carrier generation are poised to play an important role in the development of solar cells.\textsuperscript{1,2} Semiconductor nanoparticle architectures on surfaces have been used to assemble photoelectrochemical cell\textsuperscript{3} to tailor light emitting diodes\textsuperscript{4} and in the fabrication of chromic devices\textsuperscript{5}. However, a major challenge in the development of high-performance QD solar cells lies in the effective separation of photogenerated electron–hole pairs and the transfer of the electrons/holes to the electrode. Therefore, numerous efforts have been made in the past to include the introduction of nanomaterials with suitable band energy as efficient acceptors.\textsuperscript{6,7}

Carbon nanotubes (CNT) have attracted great attraction as potential electronic materials because of their unique one-dimensional tubular network structure on a nanometer scale and appropriate band energy. A unique feature of these materials is the variety of their band structures being either metallic or semiconducting depending upon the chirality and the diameter of the tube.\textsuperscript{8} Field-effect transistors (FETs) based on semiconductor CNTs have attracted much interest due to their superior properties such as high conductance, high mobility, and chemical inertness, compared to ones based on conventional semiconductor materials. Single walled carbon nanotube (SWNT) is an ideal candidate as a channel for collecting and transporting charges across light
harvesting assemblies. CNT in combination with NCS, which are optically or electrically active, is a topic of great technological significance due to potential synergic effects.\textsuperscript{9, 10} Studies have been focused on establishing synthetic strategies and characterization of the composite systems. These include carbon nanotubes in contact with TiO\textsubscript{2}, SnO\textsubscript{2}, and CdSe.\textsuperscript{11} CNT/NCS composites are very crucial in allowing the electrical contact between the two components and are promising materials for photovoltaic devices. The electrochemical preparation of a bis-aniline-crosslinked CdS nanoparticle–carbon nanotube matrix on electrode surfaces has been reported. The enhanced photocurrents in the CdS NP–CNT composite were attributed to the trapping of the photogenerated conduction-band electrons in the semiconductor NPs by the CNTs and their effective transport to the electrode, a process that facilitated charge separation.\textsuperscript{12} CdSe nanostructures have been studied extensively due to their suitable bandgap (1.74 eV) for visible light absorption, tailored structure and morphology, and potential applications in photovoltaic and optoelectronic devices.\textsuperscript{13-15} There are papers in the literature, wherein CdSe nanoparticles have been grafted onto CNTs to form hybrid structures with strong electronic interaction.\textsuperscript{16-18} In this paper we report the FET characteristics of photo induced charge transport in ZnS nanocrystals decorated SWNT hybrid system. ZnS is an important wide band gap semiconductor, which is widely used in photodetectors.\textsuperscript{19} These $n$-type ZnS NCS caped with mercaptopropeonic acid (MPA) are attached to $p$-type semiconductor SWNT through an organic molecular linker 1-pyrenemethylamine via carbodiimide, a zero-length coupler. We have discussed in detail the role and contribution of a linker molecule, pyrene, towards the total photoresponse obtained in the ZnS-
pyrene/SWNT hybrid system under UV illumination. This was systematically investigated by the measurement of real time photoresponse in conjunction with $I-V$ and FET transfer characteristics.

**A.2 Experimental Details:**

The SWNTs were aligned by placing 0.2 µl of SWNTs suspension between the gaps of the gold electrodes, followed by applying 0.36 VRMS at 4 MHz frequencies until a desired resistance was achieved. Detail device fabrication and SWNT alignment processes are available in chapter 2. An aqueous solution of mercaptopropeonic acid (MPA) caped ZnS nanocrystals of 5-6 nm size was prepared for ZnS functionalization of Pyrene/SWNT. Pyrene/SWNT was treated with 1 mg mL$^{-1}$ aqueous solution of ZnS (MPA) nanocrystals containing 0.1 M $N$-(3-dimethylaminopropyl)-N’-ethyl carbodiimide (EDC) and 0.05 M $N$-hydroxy succinamide (NHS) to obtain the ZnS-pyrene/SWNT hybrid system. The $I-V$ measurements and FET characteristics were performed using a HP4155A (Agilent, Santa Clara, CA, USA) semiconductor parameter analyzer. The real time photo response of the device with and without ZnS NCS was continuously measured after 0.1 seconds simultaneously for the 4 devices in a single chip by using Keithley 236 source measurement unit controlled by custom made Lab View program. An ultraviolet mercury lamp (160 W) was used as the UV light source (Mark 560, Martronic Co.) for photoresponse studies.
Results and Discussion:

The device fabrication was monitored by recording the current-voltage (I-V) characteristics from −0.5 V to +0.5 V at each step of surface modification of the aligned SWNT device, as shown in figure A.1. The current in the SWNTs device at a given voltage decreased upon functionalization with organic molecule, 1-pyrenemethylamine, due to a π-π stacking interaction of SWNT with pyrene groups. This further followed by another decrement in the current upon covalent coupling of 1-pyrenemethylamine with ZnS NCS through a capping agent MPA via carbodiimide coupling reaction. These changes in resistance are attributed to the reduction in the positive charge carriers (holes) in the p-type semiconductor SWNT due to accumulation of negative charges on SWNT from electron donating amine group and negatively charged MCA caped ZnS NCS on coupling with SWNTs. This has further been confirmed by taking the SEM images of the surface modified device, which shows a fine coverage of ZnS NCS well over the surface of SWNT (Figure A.1, inset).

Figure A.2 shows current-voltage (I-V) measurements performed in ambient condition on ZnS-pyrene/SWNT device (Figure A.2, inset) under dark and UV illumination. This I-V characteristic shows an apparent increase in current upon UV illumination. This has further been elucidated in a real time photoresponse measurement and an apparent increase of about 32% ΔI/I₀ in current response, defined as the difference between the illuminated and dark current value, was obtained under UV illumination (Figure A.3a). As evident from the figure A.2, the system shows a voltage dependent
photocurrent response with zero current at no bias voltage. The non-appearance of photovoltaic effect may be attributed to the non-separation of photo induced positive and negative charges for a sufficient time to generate a voltage difference. This is also evident from the slow rise of photocurrent with initial fast process of charge transfer from ZnS to SWNT due to slow regeneration of ZnS, as reported earlier in a CdS/SWNT nanocomposite. A slow photocurrent response time of about 150 seconds, under light illumination, is in agreement with a sluggish photocurrent response of 600 seconds found in a similar recently reported CdSe-Pyridine-SWNT FET and other NCS/SWNT device. This kind of photoresponse behavior of ZnS/SWNT hybrid device is found to be different from the results obtained in a similar CdSe/SWNT device reported earlier, wherein, there was an increase in the apparent resistance upon light excitation attributed to electron transfer from CdSe to CNTs and a decrease of hole concentration in the CNT network. However, the photoresponse characteristics obtained in the present work are in agreement with the recently reported photoresponse in CdSe/SWNT and CdS/SWNT hybrid systems, showing a decrease in resistance with photo-excitation. A possible explanation of charge transfer carriers (electrons or holes or both) to SWNT has been given for the apparent increase of photoresponse current. Li et al. have reported that the introduction of amine molecules (oleylamine) to SWNT results in opening of the SWNT n-channel and hence making the electron as a major carrier in CdS/SWNT hybrid system. However, we do not find any change in the p-type semiconductor characteristics of SWNT either upon 1-pyrene amine functionalization of SWNT or on ZnS functionalization in the subsequent step. On the basis of photoluminescence,
Jeong et al. have also reported that the majority charge carriers are electrons donated from CdSe NCS, though the FET characteristics of the device shows a $p$-type semiconductor property of SWNT where positively charged holes are the majority charge carriers.\textsuperscript{16} We measured a gate voltage dependence of the normalized source-drain current ($I_{sd}$), at $V_D$ of 1.0 V for ZnS-pyrene/SWNT device under dark and UV illumination (Figure A.3b). It was observed that normalized $I_{sd}$ increased under UV illumination with a significant positive shift in threshold potential with respect to dark condition, showing electrostatic gating effect with increased holes density in SWNT-channel. The increase in hole density in SWNT was calculated by the expression $C \Delta V_T / e L$, where $C$ is the approximate capacitance, $\Delta V_T$ is the shift in threshold voltage, $e$ the electron charge, and $L$ the channel length\textsuperscript{24} and the field-effect mobility of the holes was calculated in the linear regime by the eqn., $\mu = (L)^2 (dI_{sd}/dV_g) / CV_D$, wherein $V_D$ is the drain voltage\textsuperscript{25}. The device depicts an increase in holes concentration by $8.3 \times 10^6$ cm$^{-1}$ after photo excitation, as the threshold voltage was shifted to positive side by 5.5 V with respect to dark condition with a charge mobility of $\sim 1.2 \times 10^4$ cm$^2$/Vs. It is interesting to note, that the FET shows an electrostatic gating effect with no change in the transconductance (slope of FET curve) before and after the UV light illumination of the ZnS/SWNT device, indicating no change in hole mobility on light illumination, thus does not reflect any impact on photoresponse time. These results indicate that the photo induced positive charge holes are accumulated near the $p$-channel of SWNT in the photoresponse of ZnS-pyrene/SWNT.
The nonappearance of perfectly straight line in $I$-$V$ characteristic curve of device in figure A.2 indicates a contact resistance between the Au electrode and SWNT, wherein a high work function of Au electrode allows the injection of holes to SWNT, showing a p-type FET characteristic.\textsuperscript{26} The photo-induced charge transfer mechanism may be explained on the basis of work functions of ZnS semiconducting nanocrystals and SWNT, which are 7.0 eV\textsuperscript{27} and 4.8 eV\textsuperscript{28}, respectively. The higher work function of ZnS NCS facilitate the acceptance of electrons from SWNT and subsequent transfer of photo-induced positive charge carriers (holes) to SWNT, thereby increasing hole density in SWNT channel, resulting in photocurrent response, as depicted by FET characteristics. This is in contrary to charge transfer mechanism obtained in a similar CdSe-Pyridine-SWNT FET, wherein the lower work function of CdSe Q.D. results in a transfer of electrons from CdSe to SWNT.\textsuperscript{16}

Since pyrene is a fluorescent organic molecule\textsuperscript{29}, we investigated its possible contribution, if any, towards the total photoresponse of the device. Figure A.3c shows the real time photoresponse of pyrene/SWNT under UV illumination, which also displayed the same trend of increased current response as obtained in ZnS-pyrene/SWNT device, indicating an active photo excitation under UV illumination. The photocurrent increased by 17\% $\Delta I/I_0$ with respect to dark, which is about half the value of the total photocurrent response obtained in ZnS-pyrene/SWNT device, under identical condition. FET transfer characteristics study to know the type of charge transport carriers in the device showed (Figure A.3d) a significant positive shift in the threshold voltage under
UV illumination. A positive shift of 1.9 V in the threshold voltage corresponds to an increase of hole density by $3.6 \times 10^6 \text{cm}^{-1}$ in SWNT under UV illumination. This increase in photo-induced holes density in SWNT in FET transfer characteristics is consistent with the result obtained in real time photoresponse study. However, to confirm this increase in photocurrent response and positive charge transport in pyrene/SWNT device, we have done a control experiment with SWNT only, under identical conditions. Inset of figure A.3d shows no significant change either in real time photocurrent response or FET charge transfer characteristic under UV illumination, indicating a photocurrent generation only by pyrene and ZnS nanoparticles in ZnS-pyrene/SWNT device.

**A.4 Conclusions:**

In conclusion, we have characterized systematically the photocurrent response properties in conjunction with FET charge transfer characteristics in ZnS-pyrene/SWNT device. It has been observed that both the pyrene organic molecules and ZnS nanoparticles contribute to the total photocurrent response of the device. The FET characteristics of the device revealed that the photocurrent response is governed by the accumulation of photo-induced positive charge holes, which are the majority charge carriers, near the p-type semiconductor SWNT.
A.5 References:


10. Lee, H.; Yoon, S. W.; Kim, E. J.; Park, J. In-Situ Growth of Copper Sulfide Nanocrystals on Multiwalled Carbon Nanotubes and Their Application as Novel Solar


20. Rajesh; Das, B. K.; Srinives, S.; Mulchandani, A. ZnS nanocrystals decorated


Figures:

![I-V characteristics of the bare SWNT, Pyrene/SWNT and ZnS-pyrene/SWNT device. Inset, False color SEM image of ZnS functionalized SWNTs.](image)

**Figure A.1** $I$-$V$ characteristics of the bare SWNT, Pyrene/SWNT and ZnS-pyrene/SWNT device. Inset, False color SEM image of ZnS functionalized SWNTs.
Figure A.2 $I$-$V$ characteristics of ZnS-pyrene/SWNT device measured in the dark and under UV light illumination. The inset shows the configuration of the ZnS/SWNT FET device.
Figure A.3 The on/off photocurrent response of ZnS-pyrene/SWNT as a function of time under UV light illumination (a); typical gate voltage dependence of the normalized source-drain current $I_{sd}$ at $V_D$ of 1.0 V for ZnS-pyrene/SWNT device under dark and UV light (b); The on/off photocurrent response of Pyrene/SWNT as a function of time under UV light exposure (c); typical gate voltage dependence of the normalized source-drain current for pyrene/SWNT device and bare SWNT (inset) under dark and UV light (d).