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Chapter

Functionalized Carbon Nanotubes for Detection of Volatile Organic Pollutant

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Abstract

Ever since carbon nanotubes were discovered, it has attracted researchers from all corners due to the fascinating characteristics they offer. Detection of environmental pollutants is one of the prominent sectors where carbon nanotubes have been extensively applied. Pristine carbon nanotubes attracted sincere attention at the initial phase; however, the inherent shortcomings as a chemical sensor were immediately recognized. Thereafter, improvement of selective and sensitive behavior of carbon nanotubes toward varied class of analytes has remained a core area of carbon nanotube-based research. Tailoring/covering sidewalls of carbon nanotubes with different functionalizing entities has shown remarkable outcomes in improving behavior of nanotube sensors in various domains. Organic conducting polymers, macrocyclic compounds, metal organic frameworks, metal nanoparticles, etc. have been extensively reported to functionalize carbon nanotube surface. This chapter discusses porphyrin-functionalized single-walled carbon nanotubes that are found to be selective toward volatile organic compounds, and most importantly, good selectivity and sensitivity have been observed for selected group of analytes.

Keywords: carbon nanotubes, porphyrin, volatile organic compounds, sensor, chemiresistor

1. Introduction

Environment encompasses all living and non-living things coexisting with invisible strings at balance. "Pollution" is a major component that disturbs this balance and a serious threat to environmental ecosystem. Human practices exercising untowardly comfort are adding up to the existing lot of "pollutants," and this is causing adverse effects on all living creatures. Some of the dominating pollutants that are human activity generated include oxides of sulfur and nitrogen, mono- and di-oxides of carbon, particulate matter, and volatile organic compounds (VOCs).

Out of the major air pollutants, VOCs cover a large area of chemical species that are present in nature. This class of pollutants is ubiquitous in nature and also copious in amount. Most of the VOCs are colorless, having a sweet smell. Although this odor is pleasant, inhalation of the same is very harmful to health. Even at room

temperature, VOCs are present with high vapor pressure which is the cause of their volatile nature. High concentration of atmospheric VOCs degrades the air quality. When atmospheric VOCs get added to the rain water, the aqueous as well as terrestrial surroundings get polluted.

The classification of VOCs can be done according to their composition like (i) aromatic hydrocarbons (e.g., benzene, toluene, xylene), (ii) aliphatic hydrocarbons (e.g., hexane), and (iii) oxygenated compounds (e.g., ketones, acetone). According to their toxicity level [1], VOCs are categorized as follows: (i) extremely hazardous that shows adverse effect upon exposure even at low concentration of occurrence (e.g., benzene); (ii) class A compounds that may cause significant harm to the environment (e.g., acetaldehyde, aniline, benzyl chloride); and (iii) class B compounds that have lower post-exposure effects.

VOCs are dominant in industries as major solvents especially in the production of cleansers, paints, glues, carpets, rubbers, furniture, varnishes, wax, cosmetics, and air fresheners. Therefore, these products become the major sources of their emission. Also, fuel combustion and vehicle combustion have been found to be most prominent sources of VOC emission. Several types of foods and plants are also critical sources of VOCs.

Although VOCs are having many applications in our day-to-day life, their exposure is harmful. Small-scale exposure to VOCs causes ocular and throat irritation, vomiting, nausea, headache, loss of coordination, skin allergy [2–4], etc. Chronic effects that have been observed with VOCs include damage to the liver, lungs, kidney, reproductive system, respiratory system [5], and central nervous system in human beings. It is well known that some of the VOCs are carcinogenic [6, 7] too. Long-term exposures to VOCs are often deadly for all living organisms. Several VOCs (such as methane) are the main contributors of global warming. In addition, there are some VOCs that play a key role in destroying the stratospheric ozone. Because of the depletion of ozone layer, harmful ultraviolet radiations (280–315 nm) emitted by the Sun enter the atmosphere which is a potential cause of skin cancer [8] in most of the cases. When plants are continually exposed to the VOCs, it is generally observed that they suffer from slow stem growth and infertility in respective species. Also, flower and fruit growth is affected upon exposure to VOCs [9]. These data may not fully cover the scopes of damage caused by VOCs but may be sufficient enough to realize the need of some protective measurements against exposure to VOCs.

It is accepted that there should be all-out effort at war footing to curb the root causes of VOCs emission, yet, at the same time, reliable means are required to ensure a safe level of inhabitancy. As efficient control of VOC emission is a tough deal, exposure of the same to living systems is certain and obvious. In such cases, it is necessary to get real-time information of their concentration in the environment so that safety measures could be adapted in time to avoid potential hazard. To design some safety measure, reliable detection of VOCs at their permissible exposure limit (PEL) concentration is very necessary. There are three standard ways of reporting the concentrations of VOCs: (i) the concentration of individual VOCs; (ii) the sum of the concentrations of specific, individual VOCs in a sample; and (iii) as total organic carbon (TOC), which is the concentration of organic carbon in the gas stream. The concentrations are expressed in milligrams per cubic meter (mg/m^3). For TOC monitoring, among the most widely accepted techniques are flame ionization detectors (FIDs), catalytic oxidation, and photoionization detection (PID). For monitoring of individual VOCs concentration—(i) sorbent tube followed by gas chromatography (GC) separation [10–14], (ii) non-dispersive infrared (NDIR) detection [15–17], (ii) differential optical absorption spectrometry (DOAS) [18], (iv) Fourier-transform infrared (FTIR) spectroscopy, and

(v) mass spectroscopy [19] are among the mostly used standard techniques. The reliability, precision, and sensitivity of most of these techniques are unquestionable. However, limitations are there in terms of inherent delay between sample collection and measurement/analysis. The typical procedure of detection of VOCs with these techniques starts from sample collection from the affected sites which would be stored in canisters/Teflon bags, and then analysis of the samples is carried out in the laboratory environment. Thus, possibility of degradation of sample and incapability of accessing real-time data are inherent shortcomings, even with these most powerful analytical tools. Moreover, direct-reading analytical instruments such as FID and PID detectors do not only respond to VOCs but also to other organic compounds. As these instruments are calibrated with only one compound, the signal represents all compounds of the mixture as an equivalent of this compound. The output signal gives no information about the qualitative composition of the mixture. More profusely, all the abovementioned techniques are very costly and require continuous consumable and trained manpower. Gadgets that are capable of real-time monitoring come costly and are usually not very user-friendly.

Therefore, there is a need of some reliable, efficient, cheap, and user-friendly detection device for the real-time monitoring of the VOC level toxic air.

Sensors constitute the intelligent class that can be useful for the detection of VOCs as they are capable of transforming some change in a target physical/chemical quantity to any format of signals that are easy to be read or logged [20]. For an efficient operation, a sensor should be:

  i. highly sensitive,

  ii. highly selective,

  iii. durable,

  iv. of small size,

  v. handy, and

  vi. with operation ease.

Taking into consideration all of the above points and in order to obtain efficient sensing, it is very important to choose proper sensing platform, appropriate sensing materials [20–21], and optimized synthesis parameters.

To apply a sensor for

  i. real-time monitoring of the VOCs,

  ii. efficient power management, and

  iii. enhancing the mobility of the sensing gadget,

it is essential to minimize the size of the sensor or, more comprehensively, the sensor backbone. The use of nanomaterials or, more precisely, carbon nanotubes (CNTs) is a perfect solution in order to control the physical footprint of the sensor.

In this chapter, CNT-based VOCs sensors, especially in chemiresistive modality, will be discussed. A detailed review of porphyrin-/metalloporphyrin-functionalized CNT-based VOC sensing has also been provided.

2. Carbon nanotubes

Carbon is the most versatile element in creation. The structural and characteristic specialties of carbon nanotubes are defined again, by the fascinating features of carbon atom. Carbon exhibits three allotropes in solid phase, viz. diamond, graphite, and Buckminsterfullerene [22] that show extreme contrast in their behavior.

CNT is made up of a seamless rolling of graphite sheet. During rolling up of a graphite sheet, σ-π rehybridization takes place due to the formation of a curvature resulting in π confinement. The high electrical conductivity of CNTs finds its root at this π-confinement. CNTs can be classified into three types on structural basis, viz. (i) single-walled carbon nanotubes (SWCNTs) that are hollow cylinders of individual graphene sheets, (ii) multi-walled carbon nanotubes (MWCNTs) that are group of coaxial CNTs, and (iii) double-walled carbon nanotubes that are group of two coaxial CNTs. The last type (i.e., DWCNTs) did not find much technological importance in contrast to the other types. Iijima, in 1991, observed MWCNTs for the first time [23] followed by independent and simultaneous observation of SWCNTs in 1993 by Iijima [24] and Bethune [25].

In order to maintain tubular structure during formation from a graphite sheet, SWCNTs should have at least 0.4 nm and at most about 3.0 nm diameter [26, 27] as suggested by structural calculations. A larger diameter SWCNT has a strong tendency to collapse, unless it is supported by other force or surrounded by neighboring force as in MWCNTs. Such low cross-section results in electron confinement and reduction of phase space for scattering that result in low scattering probability and high mobility for charge carriers. These facts indicate toward a faster charge transduction in CNTs, and while operating as a gas sensor, such characteristics reduce the response time for CNT-based sensors significantly. Excellent mechanical/thermal properties and chemical stability [28] also allow CNTs to withstand harsh operating conditions. However, the highest advantageous aspect of the 1-D nanostructure of CNTs lies in absolutely high aspect ratio with the diameter of few nanometers and lengths up to 100 microns that results in the presence of almost all atoms on the surface of the tube. Such molecular wires [29], with excellent quantum confinement, are extremely sensitive to local environment since any local charge can drastically modulate the carrier concentration along 1-D wire axis. Thus, CNTs are considered among the most potent nanostructured sensing elements.

The circular curvature in CNTs results in σ-π rehybridization. Three σ bonds, therefore, remain slightly out of plane, and automatically, for compensation, the π-orbital is asymmetrically distributed inside and outside the wall of nanotube (as depicted in **Figure 1**) [28].

A rich π-electron conjugation is thus formed due to the distorted electron cloud, outside the nanotube structure, rendering high electrochemically active surface. Any electron-donating or electron-withdrawing entity (e.g., NO_2, NH_3, O_2) finds it easy to either donate or withdraw electrons from CNT surface, thereby modulating
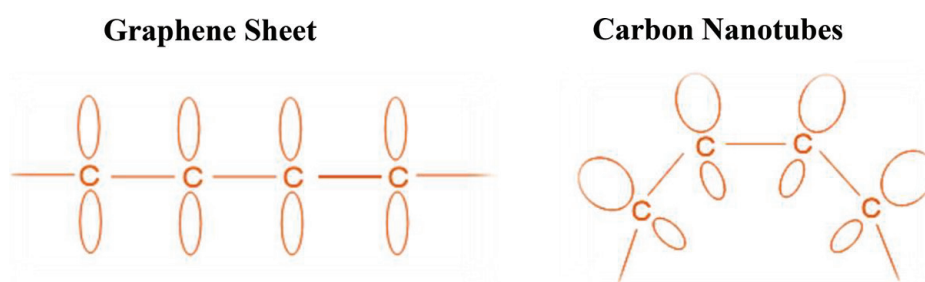
Figure 1.
π electron conjugation in graphene sheet and CNT.

overall electrical resistance [30–31]. Fundamental sensing mechanism during interaction of CNTs with electron-donating/electron-withdrawing analytes, therefore, can be given as below:

$$CNT + Gas \rightarrow CNT^{\delta e}\, Gas^{\delta+} \text{ or } CNT^{\delta+}\, Gas^{\delta e}$$

where δ denotes the number of charge(s) transferred during interaction.

The sensing mechanism for pristine SWCNTs, based on the above model, is quite simple, and since SWCNTs are p-type in nature, it is always easy to propose charge transfer-based sensing mechanism. Apart from attractive surface, gas molecules can be adsorbed at nanopores inside a tube, interstitials in tube bundles, and grooves above the gap between two neighboring tubes [28]. The adsorption capacity and mechanism of individual sites are unique, which may be affected by surface functionality and structural deformations [32]. It should be noted that such adsorption is succeeded by (i) charge transfer between a donor or acceptor type of molecule (or group) and individual SWCNTs, leading to the Fermi level modulation in semiconducting tubes, resulting in conductivity change [33], and/or (ii) creation of SWCNT molecule-SWCNT junction, leading to a hopping mechanism for intertube charge transfer between SWCNTs and an intertube modulation of the SWCNT network, such phenomenon being valid for both metallic and semiconducting SWCNTs [34]. Such capability, on the one hand, enhances lower detection limit for CNT-based sensors and, equally, results in strong adsorbance of the analyte, rendering poor recovery behavior. Li et al. [35] have reported almost 10 hours of recovery time for pristine nanotube-based sensors. Theoretical calculations further show that defect sites in CNTs result in stronger chemisorptions of analytes and large transfer interaction, in comparison to defect-free nanotubes.

A review of pristine CNT (SWCNTs as well as MWNTs)-based VOC sensors (this is applicable for other analytes too) shows that the limitation in sensing mechanism [36] and high surface-binding affinity to a large class of analytes possess toughest hurdles toward obtaining the best of CNTs as sensing agents. Also, Shirsat et al. [37] have suggested CNTs as not favorable platform for detection of VOCs because of lack of affinity.

In order to obtain better versatility in CNT-based sensors and to enable the same for selective sensing, a large spectrum of efforts have been carried out till date that includes (but not limited to) (i) creation of defect sites on CNT surface [38]; (ii) functionalization of CNT side wall with target-specific entities that contain conducting polymers [39, 40], metal nanoparticles [41], metal oxides [42], etc.; and (iii) formation of composites [43–45], etc. Functionalization of CNT side wall has the added advantage of improving sensor recovery characteristics since in such configuration, the analyte is not allowed to come in direct contact of CNT surface. The honeycomb structure of CNTs, along with high binding energy of gas analytes, results in slow desorption of analytes, thereby reflecting poor recovery behavior in pristine CNT-based sensors. Thus, functionalized structures of CNTs have attracted significant research interest toward alleviation of the problems of selectivity and recovery of pristine CNT-based sensors.
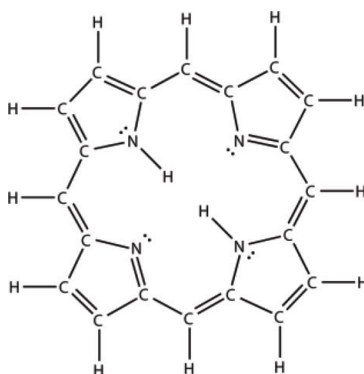
3. Porphyrins

A member of the family of macrocyclic compounds, porphyrin(s), has remained as the first preference for VOC sensing. As porphyrins show high impact on VOC sensing regime, a comprehensive study of its nature, properties, and sensing mechanism is given below.

Porphyrins and the related tetrapyrrolic macrocyclic compounds, chlorins, and corrins constitute an interesting class of macrocyclic structures that play crucial roles in nature and life [46]. Porphyrins, along with their metalloderivatives, exhibit an abundant series of physicochemical properties that enables them to cater as protagonists in flexible catalysis, especially, in the field of biology and chemistry [47]. Heme(the component of hemoglobin) and chlorophyll of chloroplasts are the examples of porphyrins that are present in nature. Nature, most beautifully, incorporates little-to-moderate changes in these macrocyclic structures to materialize the processes and versatility of life. Through the last two decades, the scientific community across the globe has witnessed abundance of examples that forward exploration of porphyrins/metalloporphyrins as building blocks for tailor-made applications [48]. The versatility in porphyrin molecular framework results in a wide range of mechanisms for analyte binding which include Van der Waals force, hydrogen bonding, π interactions, and coordination chemistry [49]. Detection of highly oxidizing/reducing gases [50], and especially odorous analytes, specific to the class of VOCs, has been reported, and these promising outcomes have triggered series of investigations toward sensitive and selective detection [51] of VOCs by porphyrins/metalloporphyrins.

The fundamental porphyrin structure (or porphine, as it is mostly called) is a cyclic tetrapyrrole ring with a highly delocalized planar network (**Figure 2**). The structure is analogous to other π—macrocycles having the characteristic central "core" which can be altered by the puckering of the porphyrin macrocycle (the range of variation of the core has been observed to lie between 2.098 and 1.929 Å).

This basic unit—a free base porphyrin (with no side substituent and no central metal ion)—has four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges (=CH—). They are sharing a macrocycle of 20 carbon atoms and 4 nitrogen atoms, to form the conjugate system. The pyrrole rings build up closed aromatic plane forming the "porphyrin nucleus." With its conjugated 18-π electron system (conforming to Huckel 4n + 2 rule), it constitutes a macrocyclic system that is known to be highly stable, even against sulfuric acid and trifluoroacetic acid [52]. The 18-π electron system is further responsible for the aromaticity of porphyrins.

The "core" of a porphyrin structure is ideal for metal incorporation. The inside ring NH protons of porphyrin are acidic in nature and can get deprotonated to give porphyrinato ions [53]. The unshared pairs of electrons, thus created, are directed toward the center of the core. The ionic radii of many metals facilitate their "fit" to this cavity by coordination bond with the four porphyrin nitrogen atoms. Such metalation gives rise to innumerable metalloporphyrin (MP) structures.

Figure 2.
Structure of porphine.

Sr. No.	Sensing material	Sensor type	VOC analytes	Concentration detected	Response recovery time	Ref.
1	Zinc-porphyrin and zinc-phthalocyanine	Optical	Pyridine, methanol	1 ppm	—	[56]
2	Tetraphenyl porphyrin	Optical	acetic acid, butyric acid hexanoic acid	855, 846, 822 ppm	10 min exposure time	[57]
3	ZnTriad porphyrin	Optical	Butylamine, hexylamine, propylamine	90 ppm	41–78 s resp.	[58]
4	5,10,15,20-Tetrakis(4-carboxyphenyl) porphyrin	Fluorescence	TNT vapor	10 ppb	—	[59]
5	Magnesium porphyrin	Optoelectronic	Methanol, propanol, ethanol, octanol, and methylbutanol	41 ppt	~300 s response time	[60]
6	Octaethylporphine-based transition-metal complexes (Ph(M),M = Co, Cu and Zn) and carbon black (CB)	Chemiresistive	Acetone, toluene, TNT	~30 ppt	~250 s response time	[61]
7	5,10,15,20-Tetrakis(4-carboxyphenyl)-21H,23H-porphyrin and its metal derivatives	Spectroscopic	Butylamine, hexylamine, hexanethiol, and dimethylformamide, acetone, diethylether	1000s of ppm	4–9 s	[62]

Table 1.
Review of some recent reports on porphyrin-/metalloporphyrin-based VOCs sensors.

The early efforts of porphyrin-/MP-based VOCs sensors employed the broad selectivity of this class to a wide range of analytes for successful implementation as electronic nose applications [54]. Through the 1980s and 1990s, most of the work on porphyrin-/metalloporphyrin-based VOC detection has been carried out through array-based detectors with the ultimate aim of mimicking the mammalian olfactory system followed by discovery of the fact that arrays of non-selective chemical sensors may show properties similar to that of natural olfaction [55].

Some reports on porphyrin/metalloporphyrin based VOCs sensing are given in (**Table 1**).

However, as a matter of utmost inherent deficiency, the electrical conductivity of porphyrins/metalloporphyrins is not adequate for electrical transduction, a fact that refrained the application of porphyrins/metalloporphyrins as chemiresistors. The alleviation routes include exercising these class of macrocycles as functionalizing entity for highly conducting backbones—most popularly, carbon nanotubes; thanks to the advancements in supramolecular chemistry.

4. Porphyrin-/MP-functionalized SWCNTs for VOC sensing

As discussed in the previous section, limited transduction mechanism available with the SWCNTs stands as a stiff constraint toward sensing applicability. At the same time, physical adsorption of analytes to the SWCNT/SWCNT bundles is

another major difficulty that needs consideration for designing of real-time sensing elements. Surface functionalization can be a facile route to alleviate these problems and has been accepted with profound research interest worldwide. Specifically designed molecular recognition layer, when employed for surface functionalization/tailoring of SWCNTs, offers selective sensing of an analyte/a class of analytes and hinders the SWCNT surface from direct interaction with analytes.

SWCNTs, functionalized with porphyrins/MPs [63–68], have attracted significant research interest during the last decade, and encouraging research outcomes on VOC sensing based on such platform has been reported. Especially, chemiresistive modality [68] of sensing by SWCNTs functionalized with various porphyrins and MPs has shown pronounced sensing results. This particular approach has widened up possibilities of real-time VOC monitoring prospect employing electrical transduction modalities.

Surface functionalization of SWCNTs/MWCNTs is carried out either by covalent or non-covalent route. Highly stable interfaces with specific matrices are offered by covalent route of functionalization, and this pathway has been extensively adapted in the field of opto-electric/electronic study of the SWCNTs-porphyrin hybrids [69–71]. Diverse range of binding entities has been covalently linked to SWCNTs that widened the adaptation and popularity range of covalent functionalization technique(s). Harsh chemical treatments are, however, a requisite for creation of favorable moieties on the SWCNT surface that cause disruption surface conjugated π-system. Applications that ask for electrical and electrochemical activity of nanotube surface to be retained specifically [72, 73], thus, cannot accept covalent functionalization modality. It is also reported that covalent functionalization results in transformation of graphitic sp^2 surface to sp^3 orientation [66]. Therefore, even if charge transfer is possible through chemical linkages, covalently functionalized SWNT surfaces miserably fall short in charge transduction sort of operations, where extensive π-π delocalization at interfacial sites is a compulsion.

Non-covalent functionalization, on the other hand, has the specific advantage in that it can be carried out under relatively mild reaction conditions, maintaining the graphitic structure of CNTs [74]. The surface electronic properties of CNTs are, therefore, retained perfectly [75], and this ensures efficient sensing prospects. Non-covalent route of functionalization is a classic supramolecular approach where various adsorption forces, such as Van der Waals force, hydrogen bonds, electrostatic force, and π-stacking interactions [76–78], are responsible for surface tailoring of SWCNTs. Initial reports of formation of porphyrin-functionalized CNTs include SWCNT functionalization in solution phase by Nakashima et al. [79] where functionalization was affected by van der Waals forces. This particular report had truly opened a new era of functionalization of CNTs by porphyrin(s). Porphyrins constitute certain attractive choices for non-covalent functionalization of CNTs with highly polarisable aromatic porphyrinic cores that interact strongly with π—conjugated graphenic sidewalls [79, 80].

Functionalized structures exhibit multifold betterment in terms of sensitivity as well as selectivity as compared to pristine SWCNTs and/or porphyrin-based sensors [66, 68]. This has proved the synergistic impact of functionalization in sensing behavior and attracted high research interest. In porphyrin-functionalized SWCNT electrochemical sensor system, the transduction characteristics of the sensors are decided by SWCNTs, whereas porphyrins or metalloporphyrins define specific affinity toward the analyte(s) [81]. The enhanced sensitivity of the functionalized platforms, as compared to pristine SWCNT-based device, results from extended π-π conjugation formed at the interface of SWCNTs. Porphyrins, on the other hand, due to variants in metal core and side substituents, show selective characteristics toward VOCs [81].

Sr. No.	Materials	Modality	Analytes	Detection range	Ref.
1	SWCNTs functionalized by phthalocyanines and porphyrin	QCM, resistive	Benzene, toluene, xylene	QCM: 60–1200 ppm Resistive: 150–1200 ppm	[81]
2	CNTs modified with porphyrin	QMB	1-Butanol	46–230 ppb	[65]
3	SWCNTs functionalized by OEP, FeOEP, RuOEP, MnOEP, TPP, RuOEP, FeOEP	Chemiresistive, ChemFET	MEK, acetone, methanol, ethanol	Percentage saturated vapors of analyte	[66]
4	Single-walled carbon nanotube-poly(porphyrin) hybrid	Chemiresistive	Acetone	50–2000 ppm	[67]
6	SWCNT-MTPP (M = Co, Ni, Cu, Zn, Fe, Cr, Mn)	Chemiresistive	Pentane, hexane, cyclohexane, acetone, MEK, 3-pentanone, MeOH, EtOH, iPrOH, MePh, p-xylene	1000 ppm except for alkanes and for amines (2000 and 300 ppm, respectively)	[82]

Table 2.
Review of SWCNT porphyrin-based VOC sensor.

Some of the latest reports , comprising of porphyrin/metalloporphyrin functionalized SWCNTs based VOCs sensor , are given in (**Table 2**):

A typical approach of non-covalently functionalizing SWNCNTs with porphyrins/MPs and their application for VOCs detection is presented below.

5. Experimental details

Sensor substrate, Si/SiO$_2$ substrates, pre-patterned with gold (Au) micro finger-tips, is a preferred platform for chemiresistive sensors. Such substrates are typically made up of four layers. The base substrate is highly doped p+ type Si with <100> orientation. 100 nm oxide layer is grown on the same by low pressure chemical vapor deposition (LPCVD). Chromium (Cr, 20 nm) and gold (Au, 180 nm) are successively deposited on the Si/SiO$_2$ substrate. Au is used as contact electrode material, while Cr serves the purpose of adhesive layer between Au and substrate. The microelectrode patterns are defined with ~3 μm gap (in this case) between nearest adjacent electrodes. Standard photolithography along with lift-off technique is employed for the purpose.
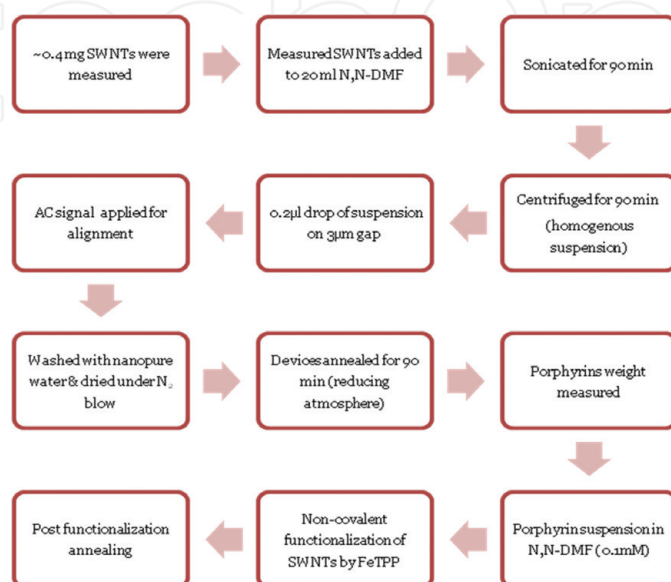
5.1 Sensor fabrication

According to the architecture of substrate and nature of the sensing material to be synthesized/deposited on substrate, the synthesis process has to be determined and optimized. For synthesis/deposition of the sensing materials, either a top-down or a bottom-up approach is adapted depending on the material and requisite level of spatial control. For the present discussion, a bottom-up approach has been adapted where the sensing material is deposited on the prefabricated microelectrode pattern

on Si/SiO$_2$ substrate that itself offers contacts for integration with measurement electronics. SWCNTs, non-covalently functionalized with porphyrins/metalloporphyrins (MPs), were applied as sensing material(s) for the present course of investigations. The following sections will comprehensively discuss the steps undertaken for the fabrication of sensors employed in the present study.

SWCNTs were incorporated in the substrate in a manner so as to bridge the 3 μm gap between two adjacent Au fingertips with SWNTs. SWNTs were AC dielectrophoretically aligned between two Au fingertips to (i) achieve a device structure that is less random and (ii) attain significant control over the device base resistance.

To obtain aligned SWCNT configuration, first of all, suspension of SWNTs/N,N-dimethyl formamide (N,N-DMF) was prepared. Concentration of SWNTs in N,N-DMF was optimized through repeated experimentation. For synthesis of the devices to be used for sensing purpose, the concentration was optimized to be ~0.4 mg/20 ml. The optimized quantity of SWCNTs were dispersed by sonication for 90 min. to achieve homogeneity at medium ultrasonic power level (VWR 100C; variable power ultrasonic bath) followed by centrifugation (R-24; Remi centrifuge) at 15000 rpm for 90 min. The centrifugation was applied to get rid of SWCNTs agglomerates that were remaining in the suspension after ultrasonication. Decanted suspension obtained after centrifugation was stocked for further use. Prior to use, a requisite amount of the stock suspension was used to be sonicated for 30 min.

To align the SWCNTs, a 0.2 μL of SWNTs suspension was used to be placed on the 3 μm gap (dispersion through microsyringe) between two Au electrodes on a chip and subjected to an optimized AC signal. The dielectrophoretic alignment circuit was set up through electrical contacts to the microelectrode patterns established via probe station (ECOPIA; EPS 1000), an electronically gated timer (a modified RADIX T48LC microprocessor controlled timer), frequency generator (Aplab; 2219-U), and a PC-controlled I/V measurement unit (CHI 660C electrochemical workstation was used for this purpose). Optimized parameters for dielectrophoretic alignment were 4 MHz frequency with 2.03 Vp-p for regulated duration (through the timer; optimized during experimentation for achieving requisite device resistance) [26]. Following alignment, devices were washed with nanopure water and dried under gentle blow of nitrogen. After preliminary drying, aligned devices were annealed at 300 °C under reducing atmosphere (5% H$_2$ and 95% N$_2$) to ensure better contact between Au pads and SWNTs.

Figure 3.
Workflow for sensor fabrication process.

5.2 Non-covalent functionalization of SWCNTs by porphyrin/MPs

After obtaining aligned pristine SWCNT network-based device, non-covalent functionalization of the SWCNTs by iron tetraphenyl porphyrin (FeTPP) was carried out. For a typical VOC sensing application, directly procured FeTPP (from Sigma Aldrich; Switzerland) were used. Solutions of desired FeTPP were prepared in N,N-dimethyl formamide (0.1 mM) by vigorous mixing (REMI; Cyclomixer CM-101) for 30 min at room temperature.

For the functionalization of aligned SWCNTs, a 0.4 μL drop of the FeTPP solution was placed over the pristine aligned SWCNT network for 30 min (optimized casting duration), followed by wash under nanopure water, and, finally, annealing in N$_2$ atmosphere for 60 min at optimized temperature for each case. **Figure 3** gives a consolidated representation of the workflow for sensor fabrication process.

6. Results and discussion

6.1 Field emission scanning electron microscopy

Field emission scanning electron microscopy image of the fabricated devices was recorded with Nova NanoSEM 450. **Figure 4** shows FESEM image of typical SWNTs-FeTPP sensor. It could be clearly observed from the **Figure 4** that the SWCNTs functionalized with FeTPP could well bridge the gap between two Au microelectrodes. The average diameter of the functionalized structures could be estimated to be ~20 nm. Encouraging part of this observation might be in terms of a facile, repeatable, and batch fabrication pathway.

6.2 Current-voltage (I-V) characteristics

CHI 660C electrochemical workstation (CH Instruments; Texas, USA) was used for studying the current-voltage (I-V) characteristic by applying the linear sweep voltametry technique (−1 to +1 V; 10 mV/s). Before performing electrical
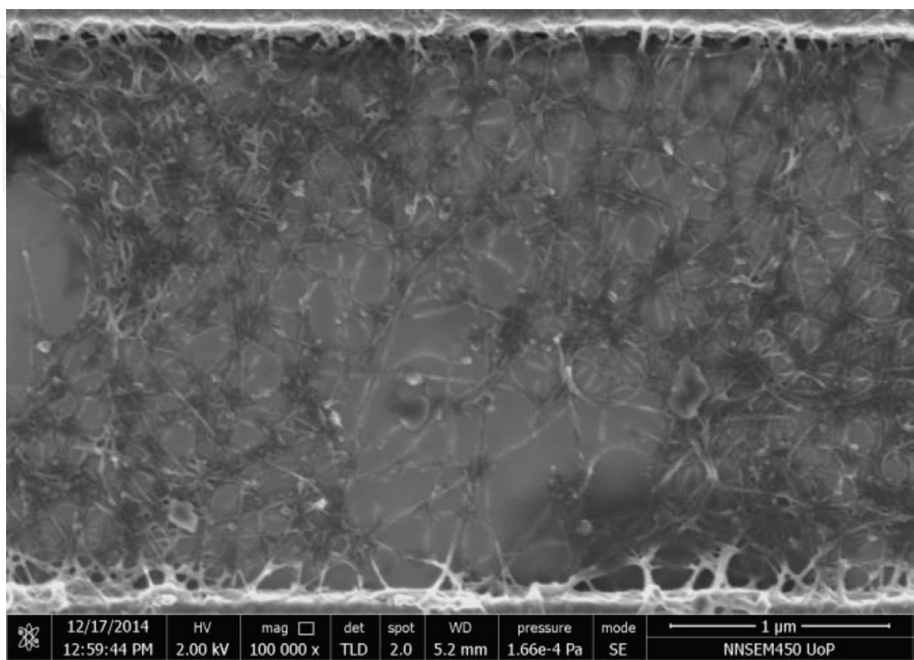
Figure 4.
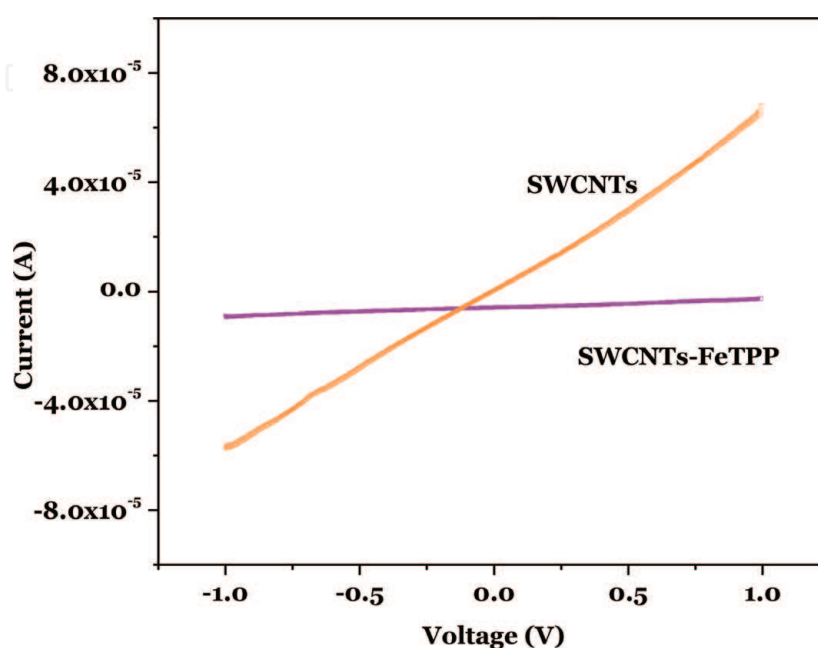*FESEM image of the SWCNTs-FeTPP sensor.*

measurements, the substrates were bonded to a custom PCB. Current-voltage characteristics of SWCNT-based devices before and after functionalization are shown in **Figure 5**. In case of SWCNT (pristine)-based sensor, current level is high as compared to functionalized sensors. **Figure 5** shows that after functionalization, decrease in current level was evident. Such decrease is attributed to the donation of electron from FeTPP to SWCNT backbone resulting in a decrease of majority charge carriers in p-type SWCNTs and creation of charge scattering sites at point of recombination [68].

6.3 Chemiresistive sensing characteristics

Chemiresistive sensing of the sensors at room temperature was carried out through a custom-built system where the sensor chip with electrical throughputs was atmospherically isolated in a flow cell (quartz c.a. 8 cc by volume). Dry air flow was employed initially through the flow cell (10–12 min) to achieve steady baseline for measurement. The fabricated sensors were exposed to various concentrations of VOCs by preparing calibrated dilution. Mass flow controllers (Alicat Scientific Inc., MC200) were employed to control the flow of both dry air and analytes. After each period of exposure, dry air was flown for sensor recovery. A constant current (5 μA; DC) was applied to the sensors, and consequent changes in potential, as a function of various concentrations of analytes, were recorded by a PC-controlled source-measure unit (Keithley 2400).

Figure 6 shows representation of normalized resistance ($\Delta R/R_0$) values for the sensors under analyte exposure of various concentrations, where ΔR representation shift of resistance value of the sensor from its baseline value and R_0 denoted the baseline resistance (the normalizing factor). Performance of the sensor(s) at four different concentrations (5, 15, 25, 35 ppm) has been reflected in terms of histogram. Performance of at least five devices has been observed for each analyte. Device-to-device variation was found to be encouragingly trivial. All analytes could be characterized with electron-donating nature [51].

The sensing performance clearly reflects the highest response for ethylbenzene, while toluene could also be detected at higher response values, in comparison to

Figure 5.
I-V characteristics of the SWCNT and SWCNT-FeTPP sensor.
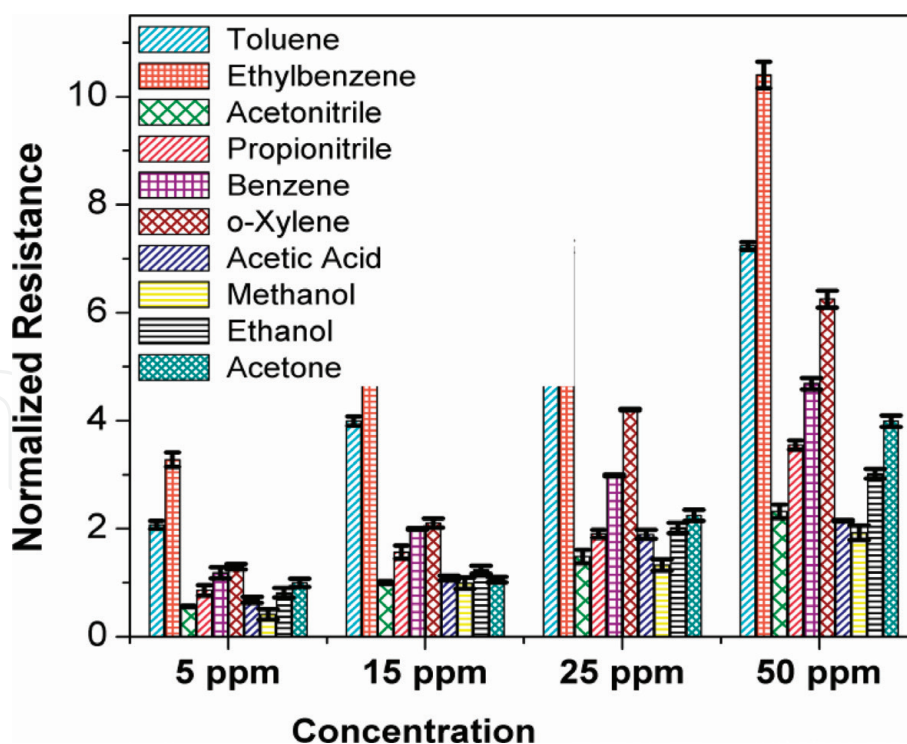
Figure 6.
Histogram of SWCNTs-FeTPP sensor toward various VOCs.

other analytes. As a common rationale, all the analytes undertaken for study have reflected an electron-donating behavior [68], and therefore, it is well envisaged that the structural signature of the analytes play important role in shaping the sensor response [83]. For example, the ethyl group present as side-substituent in benzene ring (of ethylbenzene) might have acted as a better electron donor than methyl group in toluene. Such behavior might be rationalized on the ground that methyl "carbon" of an ethyl group owns better electron density from adjacent hydrogens and is in a better position to donate. In o-xylene, the two alkyl substituents decrease effective electron density present on the central ring in comparison to toluene, resulting in lower sensing response than for toluene. The absence of any side substituent in benzene has resulted in inferior response for benzene, in comparison to its derivatives. Another issue that is pertinent from the observations is that the sensor has exhibited better performance for aromatic VOCs. Due to structural symmetry of aromatic side substituent in TPP and benzene ring, the π transitions might have been better favored. Therefore, from these observations, it is quite sure that if the structural geometry of target VOCs is properly analyzed, suitable porphyrin/metalloporphyrin can be employed as functionalizing entity for CNTs toward designing of explicitly selective VOC sensor backbones in chemiresistive modality.

7. Conclusions

Reliable detection of VOCs has remained a challenge because of the characteristics similarity among VOCs families. Porphyrin/metalloporphyrins, although, have shown prominent capacity in detection of VOCs; chemiresistor modality of sensing with this class of materials could be truly realized after CNTs were introduced in the realm. Porphyrin-/metalloporphyrin-functionalized SWCNTs have a significant potential in development of low footprint chemiresistors that enjoy simple functionality and can be embedded into standard electronics domain at less complexity, a clear advantage over porphyrin-/metalloporphyrin-based sensors that

are not operated for direct electrical measurements, for example, mass transduction, spectroscopic measurements, etc. Also, in comparison to the broad selectivity of porphyrin-/metalloporphyrin-based VOCs sensors, functionalized CNT-based chemiresistors can offer better selectivity based on the structural geometry of the target VOCs and according to the design of the porphyrin/metalloporphyrin structure. Systematic study and an affluent database generated through the same, for porphyrin/metalloporphyrin, VOC correlation, can lead to development of future olfactory type solutions for VOC detection.

Conflict of interest

There is no "conflict of interest."

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