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Calixarene-functionalized single-walled carbon nanotubes for sensitive detection of volatile amines

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ABSTRACT

Here we report a calixarene functionalized SWCNT hybrid for sensitive detection of volatile amines at room temperature. The hybrid formation was done through noncovalent functionalization of SWCNTs with calixarene using solvent casting technique, and the functionalization was confirmed through structural (SEM and TEM), spectroscopic (Raman spectroscopy) and electrical ($I_D - V_D$ and $I_D - V_G$) characterizations. The results revealed a sensitive detection for all test analytes down to 1 ppm concentrations with a sensor sensitivity of 4.1%/ppm, 7.4%/ppm and 5.71%/ppm of NH_3, TMA and DMA (commonly known as total volatile bases or TVBs), respectively. The limit of detection (LOD) of the hybrid was also found to be ~0.6 ppm, ~0.3 ppm and ~0.4 ppm for NH_3, TMA and DMA respectively. Further, the field effect transistor analyses indicated that the sensing mechanism of the SWCNT-calixarene hybrid is dominated by the electrostatic gating effect. The sensing capability of the hybrid at low analyte concentration and availability of wide variety of calixarene opens up the possibilities of development of only calixarene based SWCNT-calixarene sensor arrays for the realization of electronic nose application.

1. Introduction [1]

The detection of volatile organic compounds (VOCs) is of great significance for many applications, such as environmental monitoring, occupational health safety, food safety and medical diagnosis [2–5]. In particular, identification and quantification of volatile amine becomes crucial for determining the quality as well as the shelf life of the packaged food. Presently, the date of expiry, along with the storage instructions printed on packaged foods is an indirect indicator commonly used for determination of food freshness. However, the food products may undergo unsafe spoilage and become unsafe for human consumption due to unsafe storage/transportation, or change in packaging atmosphere, or prolonged exposure to sunlight. In fact, volatile amines or nitrogenous compounds, primarily ammonia (NH_3), trimethylamine (TMA) and dimethylamine (DMA), which are known as total volatile bases (TVBs) [6], are produced because of microbial degradation of meat/fish produces due to unsafe storage or improper handling, and are considered as the primary indicators of meat/fish spoilage [7,8]. A highly sensitive, reliable and miniaturized sensor for volatile amines could be a suitable alternative for determining the freshness of meat/fish, can serve as a determinant of shelf life of meat/fish as well as monitor the on-site of volatile atmospheric amines.

Several transduction mechanisms have been proposed as solutions to build highly sensitive and low-cost sensing platforms for an efficient sensing of TVBs and VOCs [9–13]. In this regard, a chemiresistive platform for volatile amine sensing could be an attractive substitute, because of its simple device configuration and transduction mechanism. A chemiresistor offers possibilities for miniaturization to make high-density sensor arrays with low cost and multiplexing capabilities. Likewise, various innovative-engineered materials have also been proposed as a building block to improve the sensing performance of the chemiresistor [2,6,14,15]. Among the engineered nanomaterial, one-dimensional nanostructures (e.g. nanowires, nanotubes, nanorods, nanoribbons and nanobelts) hold greater potential as compared to two-dimensional nanostructure (e.g. thin films) for the development of highly sensitive sensor because of (1) greater absorptive capacity due to high surface to volume ratio and (2) greater modulation of electrical properties (e.g. conductance, capacitance) change upon exposure to analytes due to the formation of comparable interaction zone (i.e. Debye length) with respect to the their diameter [16]. Among

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the one-dimensional nanostructures, metal/metal-oxides based nanowires showed promising sensing properties, but their use for ambient condition operation is limited due to the requirement of higher operating temperature. Single-walled carbon nanotubes (SWCNTs), a carbon based one-dimensional nanostructure, has been proven to be a good sensing material for ambient condition operations owing to its superior electrical properties and chemical stability at ambient condition [16–18]. Further, the sensitivity of the SWCNTs towards a specific analyte can be imparted through functionalization of SWCNTs with suitable molecules [19]. The functionalization of SWCNTs can be done through covalent or noncovalent modification. The noncovalent functionalization, mainly through $\pi - \pi$ interaction, allows facile functionalization almost without altering the electronic properties of the SWCNTs. Simple solvent casting method can achieve the noncovalent functionalization of SWCNTs.

Calixarene, an organic macrocyclic compound has shown its potential for use in high-sensitivity chemical sensors, typically with optical- [20,21] or mass-based [22] transduction due to its tunable chemical properties and ability to interact with analyte molecules through weak van der Waals force. The very low electrical conductivity of calixarene is the major obstacle for the development of exclusively calixarene-based chemiresistive sensors [23]. However, the SWCNT-calixarene hybrid prepared through surface modification of SWCNTs with calixarene, can overcome the issue of conductivity. In the hybrid, the superior electronic property of SWCNTs improves the conductance of the device whereas the binding ability of calixarene towards various VOCs improves the sensitivity of the device when used as a sensory layer. Further, the hybrid formation can be easily achieved through noncovalent functionalization of SWCNTs due to the strong interaction between the π-conjugated graphenic sidewall of the SWCNTs and the aromatic ring structure of the calixarene.

Calixarene has a bowl like structure with a cavity at the center, having a hydrophobic pendent and has the ability to adapt to a change from close to planar conformation upon interaction with the analyte molecule. Hence, the sensitivity of sensor may be tuned by manipulating the calixarene-analyte interaction through the selection of the appropriate kind of calixarene having different cavity size and/or different end-terminal functional group while making the hybrid. The selectivity of a sensor is another major issue for the development of reliable sensor. The selectivity issue can be resolved by building a sensor array along with an electronic hardware and a suitable chemometrics or pattern recognition software [24]. In a sensor array, multiple number of electrodes will be present with different kinds of calixarene-based SWCNT hybrids in different electrodes which can provide a response pattern while interacting with the different VOCs and the response pattern can be used/analyzed by the chemometrics to identify and quantify the analyte. Availability of wide variety of calixarene with different end-terminal functional groups and different cavity sizes depending on the number of benzene ring, and the advancement of calixarene chemistry to synthesize tailor-made calixarene provides an option to build an array of hybrid sensor using calixarene molecule only. Alternatively, a target specific recognition molecule may be introduced while making the hybrid to improve the sensor selectivity which can only bind with the target analyte molecule to provide the sensor response. Swager group has demonstrated the selective detection of xylene isomers by exploiting the capabilities of a tailor-made calixarene [25]. However, they have used calixarene-substituted polythiophene instead of only a calixarene to functionalize the SWCNTs.

Here we report, a successful fabrication of SWCNT-calixarene hybrid through noncovalent functionalization of SWCNTs with calixarene to make a chemiresistor and evaluate the sensing potential of the hybrid towards volatile amines. The chemiresistor was fabricated through dielectrophoretic alignment of SWCNTs on a prefabricated microelectrode followed by functionalization of SWCNTs with calixarene by simple solvent casting technique. The formation of hybrid was confirmed through microscopic (SEM & TEM), spectroscopic (ATR-IR and Raman spectroscopy) and electrical characterizations (current-voltage and transport measurements). Among the amines, we have chosen NH_3, TMA & DMA for our experiment, as they are the indicators of meat/fish spoilage. Room temperature sensing results toward TVBs at low concentration indicate that the hybrid can be a potential material for the development of chemiresistor for meat/fish spoilage detection and environmental monitoring purpose.

2. Experimental

Carboxilated SWCNTs (P3 SWCNT-COOH; 80–90% purity from Carbon Solution Inc. Riverside, CA, USA), *N,N*-dimethylformamide (DMF; Sigma-Aldrich), trimethylamine (Sigma-Aldrich) and dimethylamine (Sigma-Aldrich) were used as received. Certified NH_3 (100 ppm concentration in dry air) and dry air (purity: 99.998%) gas tank were brought from Airgas Inc., Riverside, CA and used for sensing experiments. The calix-4-resorcarene used here was derived from four resorcinol aromatic rings and is referred to as calixarene throughout the text. The molecular structure of the calixarene molecule is shown in Fig. S1, and the details about synthesis and characterizations of calixarene molecule is available elsewhere [26]. It is a bowl like structure in three-dimension space with a cavity at the center [26,27]. Calixarene molecules are amphiphilic in nature. Its hydrocarbon chains, known as pendants, [26] provides hydrophobicity to the molecule and its hydroxyl groups provides hydrophilicity to the molecule.

2.1. Sensor fabrication

A homogeneous suspension of carbon nanotube was prepared by dispersing 0.2 mg of commercially available carboxylated SWCNTs in 20 mL of DMF by ultrasonication for 90 min followed by centrifugation at 15000 rpm for 90 min to separate the soluble fraction from the aggregates. The supernatant was collected carefully and sonicated further for another 60 min for device fabrication.

A sensor chip (Fig. S2) consisting of five pairs of interdigitated gold-microelectrodes were fabricated using standard lithographic patterning. A highly boron-doped silicon (p-type) wafer with a 300 nm thick dielectric layer of SiO_2 was used as a substrate. The electrodes were patterned on the Si substrate using photolithography, followed by the deposition of a 30 nm thick Cr layer as an adhesion layer and a 300 nm thick Au layer by e-beam evaporation, and finally the electrode was defined by using a standard lift-off processes. The interdigitated microelectrodes have 20 fingers; 10 fingers each from both the sides with a dimension of 100 μm in length and 5 μm in width and 3 μm gap between two fingers (Fig. S2).

SWCNTs were aligned across the gaps of the electrodes by dielectrophoretic (DEP) alignment to bridge the gap between the source and the drain of the microelectrode. A drop of 0.2 μL of SWCNT solution was placed in between the interdigitated electrode gap and an AC voltage of 3 Vp–p at a frequency of 4 MHz was applied by a function generator (Wavetek, San Diego, CA) to align the SWCNTs across the electrode gaps. Manipulating the alignment time and/or varying the SWCNTs solution concentration can achieve desirable resistance of the electrodes. After alignment the electrodes were washed with nanopure water to remove the residual SWCNTs solution and dried with nitrogen. Further, the device was annealed at 300 °C for 120 min under a reducing environment of 5% hydrogen in nitrogen gas to improve the contact between the