



Short Communication

Poly(3-alkylthiophene)/CNT-based chemiresistive sensors for vapor detection of linear alkanes: Effect of polymer side chain length

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ABSTRACT

In general, alkane vapors are difficult to detect due to their non-reactive nature at room temperature. Here, we show chemiresistive sensors made of carbon nanotubes (CNTs) noncovalently functionalized with three kinds of poly(3-alkylthiophene) (P3AT), namely, poly(3-butylthiophene) (P3BT), poly(3-octylthiophene-2,5-diyl) (P3OT) and poly(3-dodecylthiophene-2,5-diyl) (P3DT). We compared the responses of sensors composed of these materials to four linear alkanes, hexane, octane, decane and dodecane. The results show that sensors with CNTs functionalized with P3ATs that have alkyl side chains with length similar to the length of the analyte alkane produced a bigger response than the case in which the lengths are different. Based on this response trend, a sensor array was made, which can distinguish different sizes of linear alkane vapors. This work facilitates the future design of CNT-based sensor arrays for distinguishing analytes with similar physical and chemical properties.

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1. Introduction

Alkanes are hydrocarbons with only single carbon–carbon bonds and no functional groups, yet alkanes are important to human beings. They are commonly used as fuels and are also widely used in industry. However, they have safety issues including explosion [1] and inhalational toxicity [2]. The Occupational Safety and Health Administration (OSHA) in the United States has regulated the permissible exposure limit of *n*-hexane to be 500 ppm [3]. Thus, a portable, low-cost, and reliable vapor sensor for detecting and distinguishing alkanes would benefit us in aspects such as detecting fuel leaks in airplanes, detecting home-made explosives made of nitrate–fuel oil mixtures, and monitoring the environmental exposure of alkanes. However, it is difficult to make highly sensitive alkane sensors due to their lack of reactivity at room temperature and they have similar chemical and physical properties. Previous research has been done using traditional instruments, such as Fourier transform infrared (FTIR) spectrometry [4], gas chromatography [5] and ion mobility spectrometry [6]. However, those methods involve expensive and bulky instru-

ments and the testing processes are time-consuming. Emerging methods have been developed using nanomaterials such as metal oxide thin films [7], gold nanoparticles [8,9], silicon nanowires [10], and organic nanofibers [11]. However, those sensors usually have specific operational requirements such as high operation temperatures, sophisticated measurement equipment, or light irradiation. Those requirements hinder the development of those sensors.

Chemiresistive sensors based on carbon nanotubes (CNTs) have attracted significant attention due to their high sensitivity [12,13], simple fabrication process [14], and simple operational requirements. To further enhance their sensitivity and selectivity, covalent [15,16] and noncovalent [17,18] functionalizations were introduced to CNT-based chemiresistive sensors. Most of these functionalized sensors work through an interaction between the sensor and the analyte such as hydrogen bonding [15], halogen bonding [19], electrostatic effect [20], and the creation of a chemical reaction [21]. However, none of those methods work in an alkane sensor because of the lack of a specific chemical functional group and the unreactive nature of alkanes at room temperature.

Here, we demonstrate chemiresistive alkane sensors based on CNTs coated with poly(3-alkylthiophene) (P3AT). P3ATs with different side alkyl chain lengths were used in this study, namely, poly(3-butylthiophene-2,5-diyl) (P3BT), poly(3-octylthiophene-2,5-diyl) (P3OT), poly(3-dodecylthiophene-2,5-diyl) (P3DT) (Scheme 1a). We have tested the responses of these

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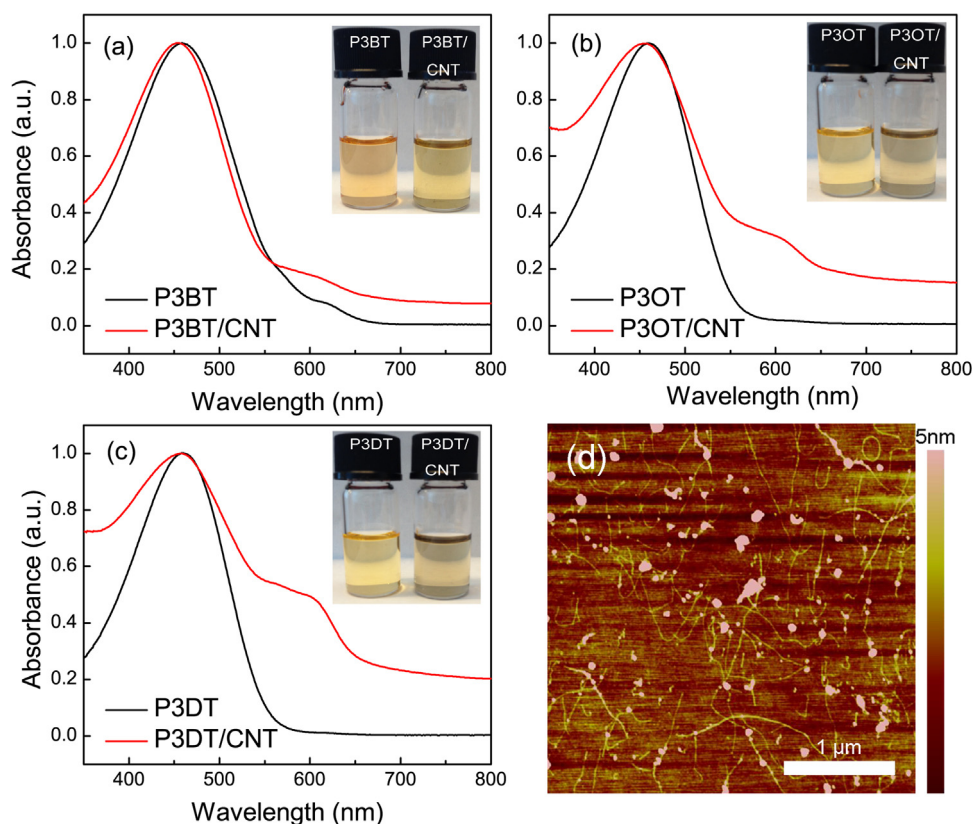
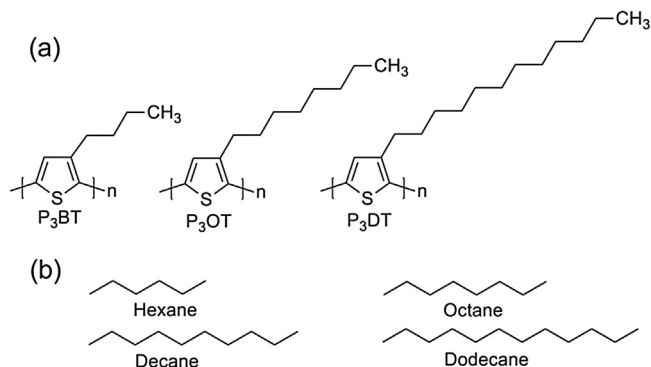


Fig. 1. (a–c) The UV–vis absorption spectra and photos of P3AT solutions (0.0075 mg/ml) and P3AT/CNT suspensions. (d) AFM image of the P3OT/CNT suspension cast on a silicon dioxide surface.



Scheme 1. Molecular structure of the three P3ATs (a) and four linear alkane analytes (b) used in this study.

P3ATs/CNT sensors to four linear alkanes, namely, *n*-hexane, *n*-octane, *n*-decane and *n*-dodecane (Scheme 1b). There are three features in our design. (1) P3ATs greatly enhance the dispersion of CNTs in solvents, which makes the fabrication process simple and repeatable. Meanwhile, good dispersion of CNT facilitates the fabrication of a continuous, uniform percolation network of CNTs, which is conducive to gas diffusion and adsorption, thereby facilitating application in vapor sensing. (2) Polythiophenes with a variety of types of side chains are commercially available so we can easily replace the polymer with different side chain lengths and other functional groups to further improve the detection selectivity. (3) The sensors are most responsive to the alkane with similar chain length as the side-chain of P3AT, a mechanism based on the general chemistry principle “like dissolves like”. This trend of response could be used to distinguish the size of alkane molecules in a vapor. This research is a proof of concept of designing a sensor array with

polymer functionalized CNTs, which can potentially distinguish similar analytes.

2. Materials and methods

2.1. P3AT/CNT preparation method

The P3AT/CNT suspensions used for making the sensors were prepared through the following steps. First, CNTs were suspended in 1,2-dichlorobenzene (ODCB) with a concentration of 1 mg/ml, followed by 2 h of sonication in a sonication bath. P3ATs were dissolved in ODCB with a concentration of 5 mg/ml. Second, the two solutions were mixed to achieve the CNT suspension, in which the weight ratio of P3AT:CNT was 3:1. The mixtures were sonicated for 2 h in a sonication bath. Subsequently, about 10 vol% of cyclohexanone was quickly injected into the mixture to facilitate the aggregation of P3ATs onto CNTs [22]. The mixtures were then kept undisturbed overnight to reach equilibrium. The mixtures thus obtained were relatively homogeneous and dark black. Since the precipitates were not removed, agitation was needed to make the suspension uniform. Third, the mixtures were agitated for several seconds and diluted in ODCB to achieve a concentration of CNTs of 2.5 μg/ml (estimated) and the diluted suspensions were sonicated for two hours. Then, the diluted suspensions were ready to use. The diluted suspensions were stable with no aggregates formed over 6 months on a benchtop at room temperature, with the exception of the P3BT/CNT suspension, which formed aggregates after a few weeks (see the photos in Fig. 1). After sonicating for several minutes, the aggregation in the diluted suspension of P3BT/CNT would disappear and the suspension would be ready to use again. These uniform and stable P3AT/CNT suspensions make the fabrication process facile and reproducible.

2.2. Sensor device preparation method

Sensors were fabricated by drop-casting one of the diluted P3AT/CNT suspensions onto pre-patterned interdigitated electrodes (IDEs) followed by heating at 120 °C for 10 min in an ambient environment to remove the remaining solvent. After the solvent evaporated, the electrical resistance of the IDE was tested. The drop-casting of the suspension was continued until the resistance of the device reached 20–200 k Ω , forming a thin film of P3AT/CNT on the IDEs. Scanning electron microscopy (Fig. S2) shows the porous and continuous structure of a P3OT/CNT thin film, which is beneficial for a vapor sensor because analyte molecules can penetrate into this thin film.

3. Results and discussion

3.1. Characterizations

UV–vis absorption spectra were obtained from the three P3AT/CNT suspensions (Fig. 1). There were additional peaks around 610 nm in the P3AT/CNT suspensions, indicating the formation of a highly ordered structure of P3ATs due to their aggregation on the surface of CNTs [23,24]. The overall baseline of the P3AT/CNT absorption spectra increased when the alkyl side chain length increases. This indicates that P3ATs with longer alkyl side chain have stronger abilities to disperse CNTs in solvent. Atomic force microscopy (AFM) was used to characterize the dispersion of CNTs. The AFM image (Fig. 1d) indicates that CNTs were individually dispersed. The height distribution study in Fig. S-1 shows that the average diameter of the CNTs in the P3OT/CNT suspension is around 1.1 ± 0.2 nm. Comparing with the manufacture's data and our previous study [25], this is an almost 40% increase of diameter from bare CNTs (0.8 ± 0.1 nm). This demonstrates the addition of the P3OT coating on the surface of CNTs. All those characterizations demonstrate the uniform coating of P3ATs on the surface of the CNTs, as well as the individual dispersion of CNTs thus produced.

3.2. Sensitivity and limit of detection to *n*-dodecane

The sensitivity of those sensors to alkane is first presented with *n*-dodecane using a P3DT/CNT sensor. Fig. 2a shows the three times repeated testing of a P3DT/CNT device by exposing to 1%, 2%, 4%, and 8% dilution of saturated vapor of *n*-dodecane (Table S1 shows the saturated vapor pressures of the four alkane analytes at 20 °C). Overall, the sensor's response to *n*-dodecane is fast, recoverable, and reproducible. Fig. 2b shows that the sensor displays a linear response to *n*-dodecane from 1% to 8%. A limit of detection (LOD) of 342 ppb was projected for *n*-dodecane following the linear fitting, and similarly a LOD of 76 ppm was projected for *n*-hexane (see supplementary materials for more detail). The LOD of 76 ppm of *n*-hexane is far lower than OSHA's permissible exposure limit of 500 ppm, demonstrating the utility of the sensor.

3.3. The effect of side chain length and the sensor array

Then, the responses of all three P3AT/CNT sensors to all four alkanes were measured. Fig. 3 shows the baseline corrected testing results. When exposed to *n*-hexane (Fig. 3a), the P3BT/CNT sensor gave the biggest response, which is about 45% larger than the response of P3DT/CNT. However, the P3DT/CNT sensor gave the biggest response to *n*-dodecane (Fig. 3b), which is about 80% larger than the response of P3BT/CNT. Fig. 3c shows the summary of the sensors' response to all the four alkane analytes. As indicated from the first arrow in Fig. 3c, the sensor response to *n*-hexane decreased as the length of the side chain in the P3AT decreased. On the contrary, the sensor response to *n*-dodecane increased as the length of

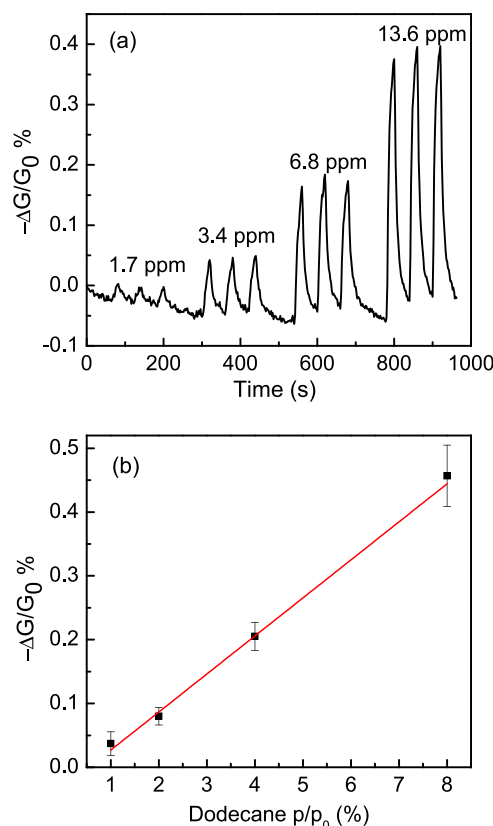


Fig. 2. (a) Real-time sensor responses to 1% (1.7 ppm), 2% (3.4 ppm), 4% (6.8 ppm) and 8% (13.6 ppm) dilution of the saturated vapor of *n*-dodecane measured from a P3DT/CNT sensor. The analyte exposure time is 20 s and the recovery time is 40 s. (b) the linear fitting of the sensor response to the vapor concentration of *n*-dodecane; data points were averaged from three independent sensors' responses.

the side chain in the P3AT increased. The responses of three kinds of P3AT/CNT sensors to water vapor were tested as well to evaluate the usage in more complex real-life situations (Fig. S4). All the sensors show much smaller response to water vapor (2504 ppm, 8% of saturated vapor) even compared with much lower vapor of dodecane (14 ppm, 8% of saturated vapor).

The different trends of response observed for the three sensors towards the alkanes vapor as shown in Fig. 3d demonstrates the capability of distinguishing the different sizes of alkanes by incorporating the three sensors into an array. Fig. 3d is the principle component score plot of the sensor array. It is clearly seen that the small alkane like *n*-hexane can be distinguished from the large ones due to the different dissolution preference into the interdigitated polymer side-chain junctions between CNTs. As the size (carbon chain length) of alkanes increases, the dependence of dissolution on the polymer chains becomes less distinct, and consequently it becomes more difficult to discriminate among the long alkanes as shown in Fig. 3d.

3.4. The sensing mechanism

The mechanism of the sensor is likely due to the swelling of P3ATs on the surface of CNTs [11,26]. CNTs form a conductive network, while P3ATs act as the insulating layer between each junction of CNTs in the network. Because the electrode gap is much longer than the CNTs, a charge must cross many of these junctions to get from one electrode to the other. When the sensors are exposed to alkane vapor, P3ATs on the surface absorb it and swell, causing spatial enlargement of the CNT junctions. As a result, the resistance of the CNT network increased and measured as a decrease in current.

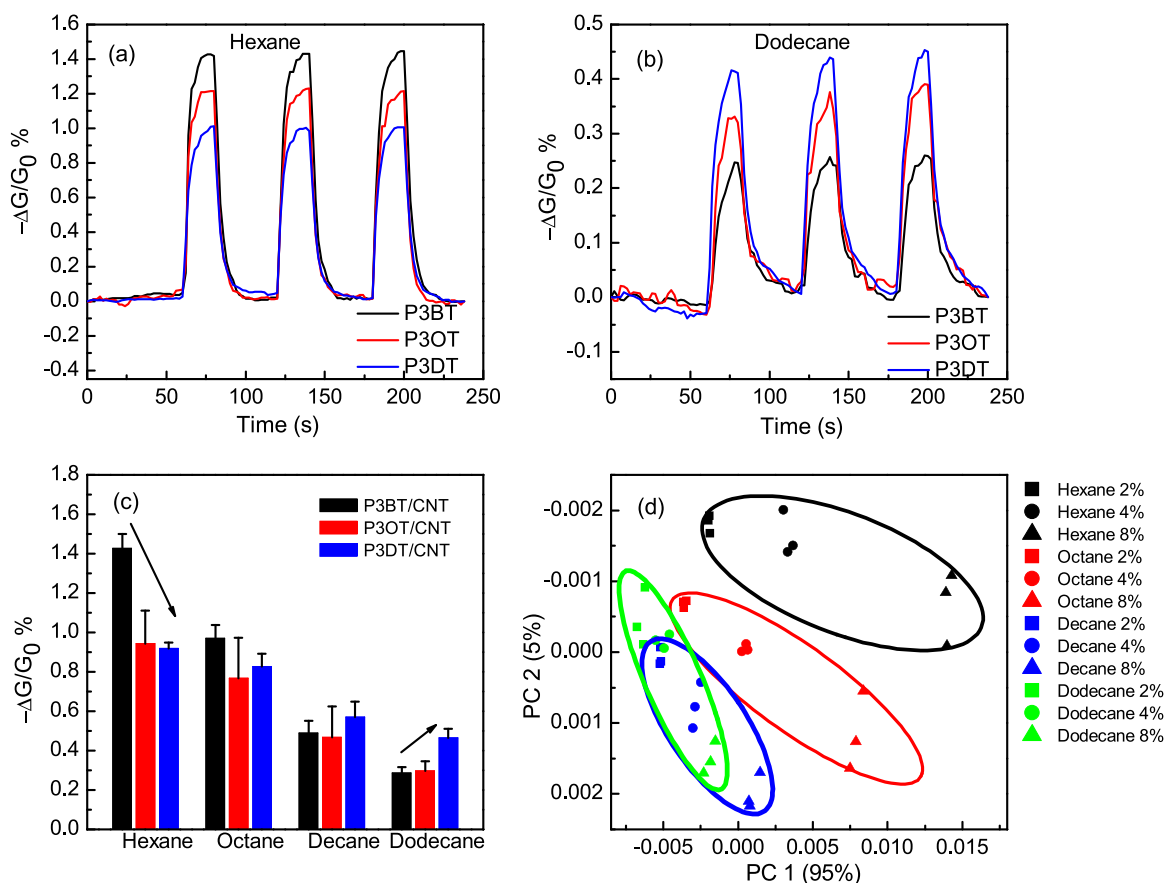


Fig. 3. (a) Real-time sensors' responses to 8% of the saturated vapor of *n*-hexane from the P3BT/CNT sensor, the P3OT/CNT sensor and the P3DT/CNT sensor. (b) Real-time sensors' responses to 8% of the saturated vapor of *n*-dodecane from the same three sensors. (c) Summary of responses from the three kinds of sensors (three independent sensors for each type) to 8% of the saturated vapor of *n*-hexane, *n*-octane, *n*-decane, *n*-dodecane. (d) Principle component score plot of the sensor array containing the three P3AT/CNT sensors to four alkane analytes (three concentrations for each analytes, three trials each concentration).

The porous structure of the CNT network thin film is easily penetrable by the vapor molecules, and the large interfacial area between adjacent CNTs in the network facilitates the sensor response. Selectivity between alkanes can be understood in two ways. First, shorter alkyl chains of P3AT are less able to accommodate longer alkanes because of their small size; hence, *n*-hexane elicits a larger response from P3BT/CNT than P3DT/CNT. Conversely, larger alkyl chains of P3AT can accommodate both small and large alkanes, but larger alkanes cause a greater disruption to the interface (*i.e.*, they cause more extensive swelling of the polymer side chains), thus leading to more pronounced sensor response.

4. Conclusions

We utilized P3ATs with three side chain lengths to detect four kinds of alkane vapors at low concentrations. The sensing results indicate that the P3AT/CNT sensors with longer side chain lengths, such as P3DT, show bigger responses to longer carbon chain analytes such as *n*-dodecane. On the contrary, the P3AT/CNT sensors with shorter side chain lengths, such as P3BT, show bigger responses to analytes with shorter carbon chains, such as *n*-hexane. Thus, by comparing the relative responses of the P3BT/CNT sensors and the P3DT/CNT sensors, we were able to selectively detect those alkane analytes within a certain range of vapor concentrations. The sensors were prepared by simply drop-casting P3AT/CNT suspensions onto IDEs. The mechanism of the response is likely due to the swelling of the P3ATs insulating layers in the conductive CNT network. Future work may involve expanding the polythiophene/CNT sensor array with other side chain functional groups, and the sen-

sor array's ability to differentiate a wide variety of analytes and interruptive vapors would be tested.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2017.03.066>.

Experimental details, height profile of the CNTs from the AFM image, SEM imaging and the calculation of the LOD.

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