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International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.7, pp 3690-3696, Sept-Oct 2014

Fabrication and characterization of poly(3-hexylthiophene) (P3HT)sensor in two techniques (Dip-coating and Spin-coating) and Sensitivity compared for various vapors

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Abstract: The gas sensors fabricated by using conducting polymer (P3HT), the poly(3-hexylthiophene) (P3HT) prepared by chemical polymerization of 3-hexylthiophene at room temperature and under inert atmosphere of N2, using hexahydrate ferric chloride as oxidant. A chemical sensor was prepared by deposition of polymer films in two techniques (Dip-coating and Spin-coating). The sensors demonstrated ppm level sensitivity and good sensitivity to various volatile organic compounds (VOCs) such as methanol, ethanol, chloroform, toluene and hexane, in concentration range of 8000-640000ppm. Direct comparison of the two sensor films with respect to sensitivity, response time and recovery time was made by measurement of the resistance changes upon simultaneous exposure to each analyte, electrical measurements showed highest sensitivity, response time and recovery time lower in technique Spin-coating compared with Dip-coating, this means the technique Spin-coating is better than Dip-coating. sensitivity decreased with sensors P3HT temperature increase in the range between 25^0C and 70^0Cin the two techniques.

Key Words: poly(3-hexylthiophene) (P3HT), conducting polymers,volatile organic compounds (VOCs).

1. Introduction

There are many chemical species of concern that must be detected, including toxic gases, volatile organic compounds, alcohol, and humidity. Various conducting polymer have been used to detect them.

To monitor of volatile organic compounds appeared to need a high-performance sensors which used to specify the type of gas or vapor and measured at room sensors which used to specify the type of gas or vapor and measured at room temperature. There are many traditional techniques managed to set the type of these vapors and measuring the concentration such as gas chromatography and mass spectrometry and ultraviolet spectroscopy, but these techniques cost a lot of money and need more time. In addition, they rarely give immediate results. Therefore, it was necessary to look for tiny and low cost sensors. Most common sensors, used in this field, are the Conducting polymers sensors such as polypyrrole (PPy), polyaniline (Pani), polythiophene (PTh) and their derivatives, have been used as the active layers of gas sensors since early 1980s [1]. In comparison with most of the commercially available sensors, the sensors made of conducting polymers have many improved characteristics. They have high sensitivities and short response time; especially, these feathers are ensured at room temperature. Conducting polymers are easy to be synthesized through chemical orelectrochemical processes. (P3HT) is one of the most promising conducting polymers, distinction easily processed, has a high charge carrier mobility [1], easy synthesis through chemical or electrochemical processes [2,5], high sensitivities, short response time[2], low coast[4] good environmental stability[1,3,8], Soluble polythiophene derivatives [10] and better electroconductivity than other conducting. (P3HT) has potential applications in many fields, such as microelectronic devices, LEDs, diodes [9], catalysts, organic field-effect transistors, chemical sensors and biosensors [6,7,9]. In this research, we used a method that relies on chemical oxidation of monomer 3- hexylthiophene (3HT) in chloride anhydrous iron FeCl3 and turn it into a Polymer (P3HT). we start preparing powder (P3HT) and characterization, then we dissolve the polymer in chloroform, 10 mg of polymer per 1 ml of the solvent (chloroform) to manufacture sensors and deposition film of (P3HT) in two techniques (spin-coating and Dip-coating), on the substrate two interdigitated metallic electrodes were priory deposited by screen printing. Afterwards, we studied the sensitivity of the sensor for (methanol, ethanol, chloroform, toluene, and hexane) at room temperature and when heating the sensor between 25^0 C and $70\ ^0$ C.

2. Experimental materials and methods

Chemicals: For the synthesis of P3HT and polymer blends, we used 3-hexylthiophene (3HT) monomer (99%), Ferric Chloride (97%), supplied by Aldrich, chloroform (CHCl3, 97%), acetone ((CH3)2CO, 99.7%), toluene (C6H5CH3, 99.9%), ammonium hydroxide (NH4OH, 28–30%) and hydrochloric acid (HCl, 36.5–38.0%) supplied by J.T. Baker and Methanol (CH3OH, 99.9%) supplied by Fermont.

Preparation of (P3HT): P3HT was obtained by direct oxidation of respective monomer using FeCl3 as oxidant at room temperature and under inert atmosphere of N2 . FeCl3 (0.025 mol) dissolved in 134 ml of anhydrous CHCl3 was slowly added to 0.0167 mol of distilled 3-hexylthiophene dissolved also in 40 ml of anhydrous CHCl3. The reaction mixture was stirred at room temperature for 25 h. The product was precipitated in methanol, filtered and carefully washed three times with methanol, hydrochloric acid (10 vol.%), acetone, NH3 or NH4OH (10 vol.%), EDTA (1 vol.%) and distilled water. The final P3HT product dried at 55 ◦C for 12 h.

Preparation of (P3HT) assensor film by spin-coating technique: After preparation ofP3HT ,dissolved P3HTin chloroform solvent, the solution concentration was 10 mg of polymer by 1 ml solvent (chloroform). The polymer films were deposited on the substrate two interdigitated metallic electrodes ,by spin-coating technique with a spin frequency of (1000,1500,2500) rpm, for (10,10,20) second respectively. After preparation of the sensor films, wash several times with distilled water, and then put it in a drying oven at temperature70^0 C under inert atmosphere of N2 for 2 hours.

Preparation of (P3HT) as sensor film by Dip-coating technique: After preparation ofP3HT ,dissolvedP3HT in chloroform solvent, the solution concentration was 20 mg of polymer by 1 ml solvent (chloroform), then dipping the substrate into a chemical polymerization solution in form vertical for 48hour, part of the polymer will be deposited onto its surface. After preparation of the sensor films wash several times with distilled water ,and then put it in a drying oven at temperature $70\ ^0$ C under inert atmosphere of N2 for 2 hours.

3. Results and discussion

3.1Infrared Spectroscopy (FTIR) :

Was recorded infrared spectrum (FTIR) of samples P3HT using spectroscopy infrared (Bruker victor 22 FTIR Spectrophotometer), where thin disks of P3HT were prepared in KBr. To ensure the drought of these samples, we had to dry the studied samples by a dryer for (12) hour in (55) ^{0}C and then record the spectra. This **Figure** 1 shows the spectrum infrared transmittance that we have got.

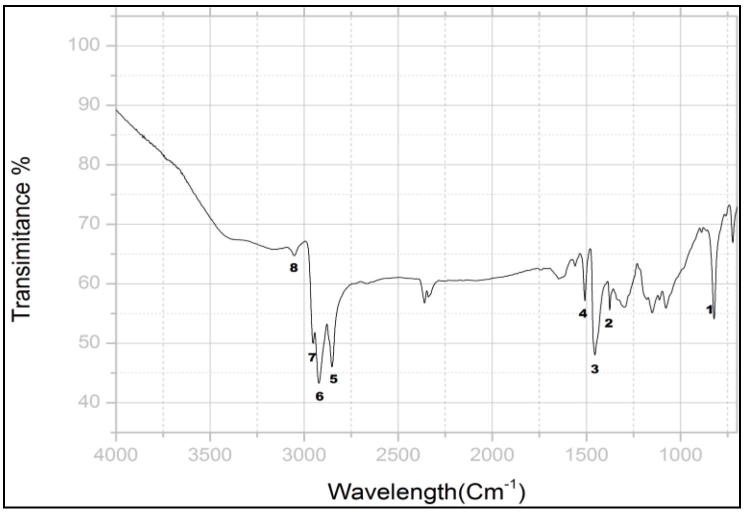


Figure 1: FTIR spectra of P3HT

Table(1) shows experimental values for the number of wavelengths of the absorption peaks and the corresponding bond, compared with the values mentioned in some reference [11,12] match with the values mentioned in the literature, which confirms we get P3HTmobility.

Table (1) Experimental values for the number of wavelengths of the absorption Peaks and the corresponding bond

Number of the function	Wavelength (Cm^{-1})	Functional Groups
1	814	**C=CH**
2	1374	**CH3**
3	1453	**C-C**
4	1506	**C=C**
5	2847	**C-H**
6	2920	**CH2**
7	2950	**CH3**
8	3052	**C=CH**

3.2 Study Sensitivity

3.2.1 Sensitivity of sensors P3HT prepared in two methods (spin-coating and Dip-coating) at room temperature for ethanol vapors

After placing the sensor in the chamber, we should wait for several minutes to ensure the stability of resistance primitive, then we inject a quantity of methanol so that we get a concentration of (40000 ppm). Then, we measure the electrical resistance of the sensor in terms of time at room temperature (T = 25°C). characterization of the sensor through the sensitivity (S) was calculated using the following equation:

$$S=\frac{Rg - Ra}{Ra} \qquad (1)$$

Ra:electrical resistance of the sensor in the air

Rg:electrical resistance of the sensor in the chamber

characterization of the sensor too through the response and recovery times of the sensor films when exposed to vapors. The former is defined as the time needed for the resistance to reach 90% of the equilibrium value, and the latter is the time necessary to return to 90% of the value read prior to exposure.

Figure 2 shows the results that we have obtained. The sensitivity in a way Spin-coating (S% = 48.2), response time 120s and recovery time 30s compared with the sensitivity in a way Dip-coating (S% = 24.4), response time 180s and recovery time 60s, observe through **Figure 2**.The sensitivity in the Spin-coating way is greater than the sensitivity in the Dip-coating way, The response and recovery time in the Spin-coating method is lower than the time in the Dip-coating way, Because the sensitivity for samples which was prepared by Spin-coating was more homogeneous and less thickness from that prepared by Dip- coating.

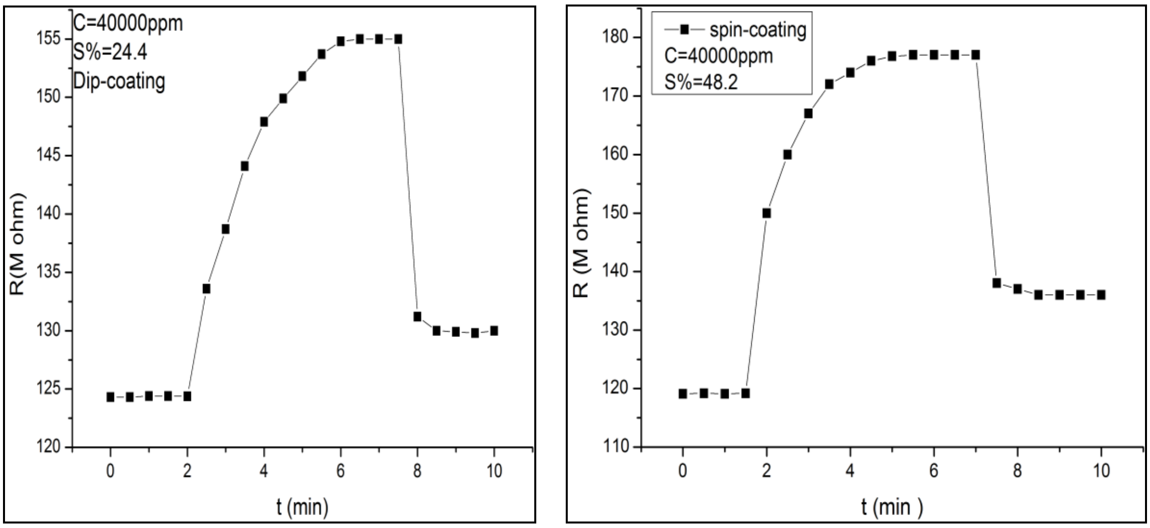
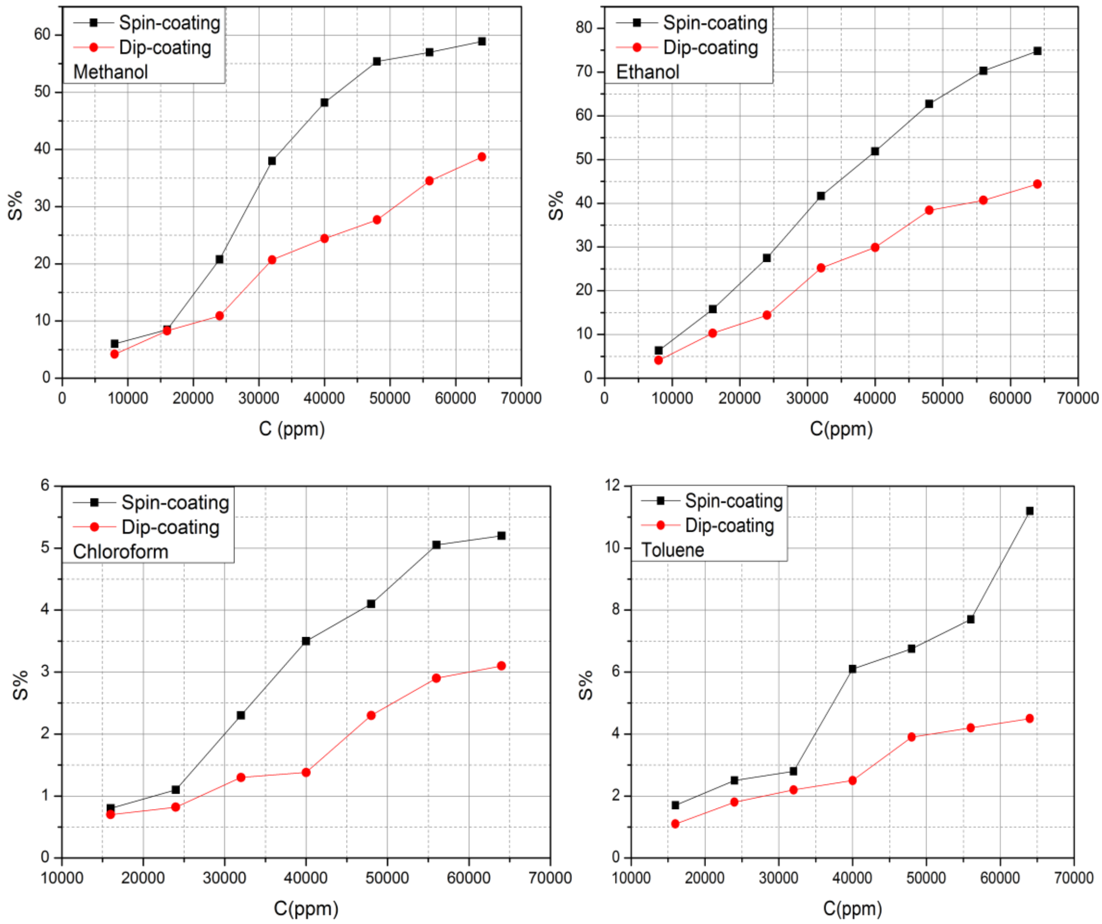


Figure 2: Cchange of resistance in terms of time for the vapors of methanol for sensors P3HT prepared at room temperature in two methods (spin-coating and Dip-coating).

3.2.2 Sensitivity compared to two methods of (spin-coating and Dip-coating)for various vapors : Figure 3shows curves of sensitivity (methanol, ethanol, chloroform, toluene ,andhexane) in terms of concentration of the sensors P3HT prepared at roomtemperature in two methods(spin-coating and Dip-coating). It is obvious that the sensitivity in Spin-coating way is better than the sensitivity in the Dip-coating way.



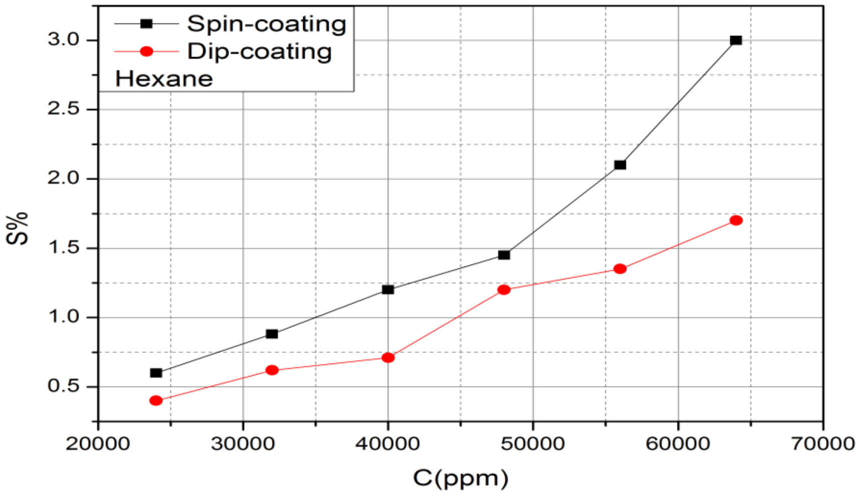


Figure 3: Change of Sensitivity in terms of concentration for various vapors for sensors P3HT prepared at room temperature in two methods (spin-coating and Dip-coating).

3.2.3 Change of Sensitivity of sensors P3HTin terms of concentration for the vapors (methanol, ethanol ,chloroform, toluene and hexane)in two methods (spin-coating and Dip-coating):

We injected different concentrations of vapors, and calculate sensitivity, we notice from the **Figure 4** that sensors P3HT prepared in a way **spin-coating** and **Dip-coating** shows high response to ethanol vapors, and a low response to hexane vapors. arrange sensitivity of vapors for P3HT filmsthat prepared in the spin-coating way and Dip-coating are as follows:

Ethanol >methanol >toluene > chloroform > hexane

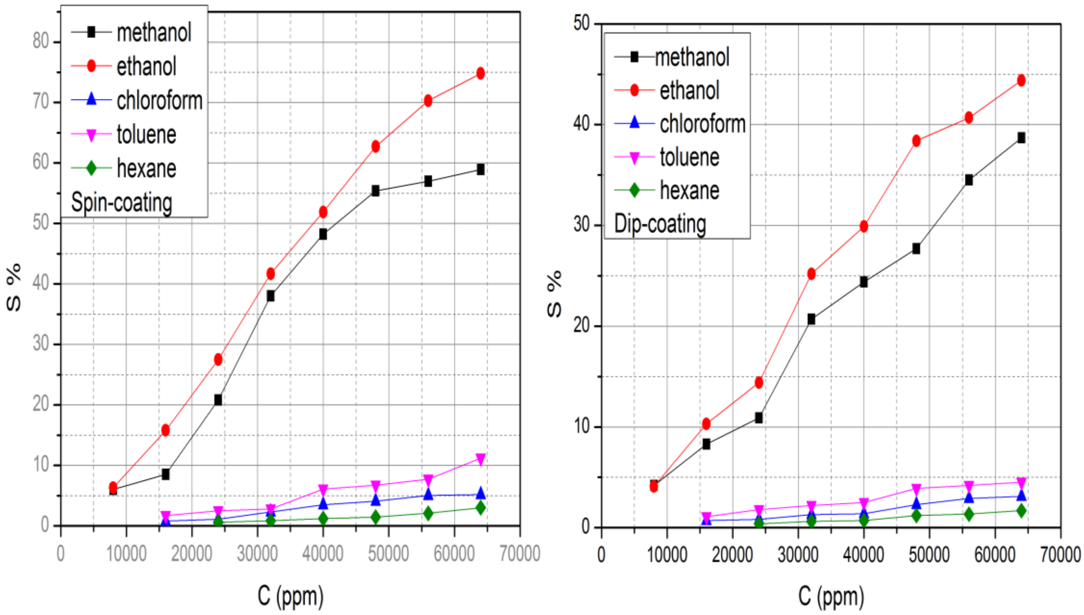


Figure 4 : Change of Sensitivity of sensors P3HTin terms of concentration for the vapors (methanol, ethanol ,chloroform, toluene and hexane) in two methods (spin-coating and Dip-coating)

3.2.4 Effect of temperature on sensitivity:

We used the previous test chamber itself, but after adding an electric heater,in which we set a sensor, so that we can change the temperature. We test a concentration of (40000 ppm) at temperatures (25,40,70)° C **Figure 5 ,6** shown the result that we have obtained.

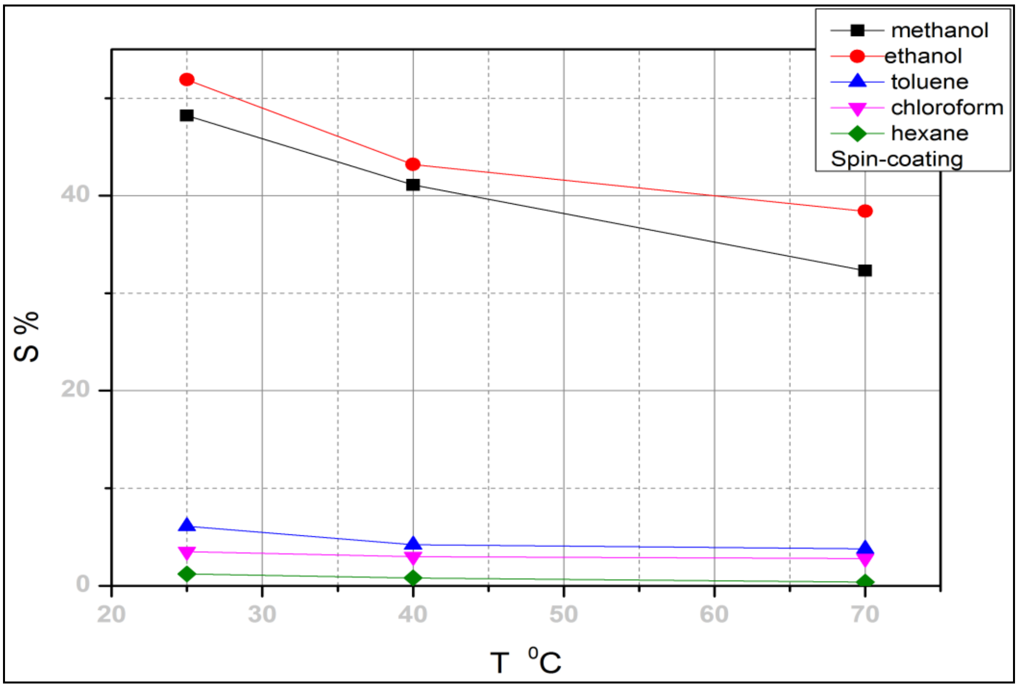


Figure 5 change of Sensitivity of sensors P3HT in terms of temperature for the vapors (methanol ,ethanol ,chloroform ,toluene and hexane) by Spin-coating.

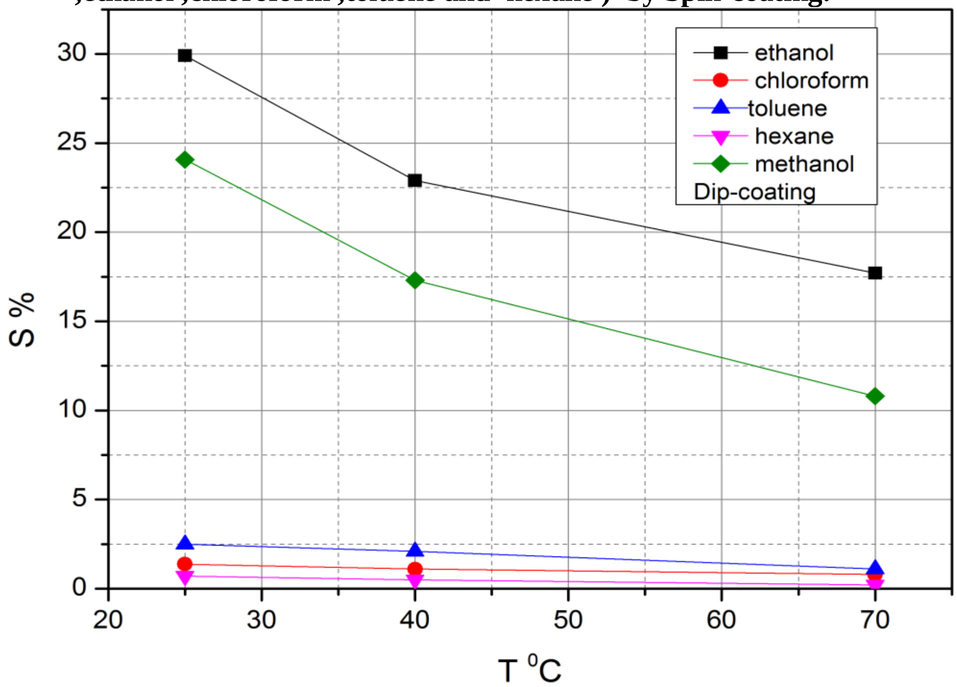


Figure 6: Change of Sensitivity of sensors P3HT in terms of temperature for the vapors (methanol ,ethanol ,chloroform, toluene and hexane) by Dip-coating.

We can notice that the sensitivity of P3HT is down by increasing the temperature. The sensitivity of P3HT depends on the formation of double links with the studied material. High temperature leads to dissociation of these links, and thus reduce the number of molecules adsorbed on the surface of P3HT which in turn leads to lower sensitivity.

4. Conclusion

Sensors based on arrays of P3HT were demonstrated to be viable options for detection and discrimination of VOCs, sensors P3HT demonstrated ppm level sensitivity and good sensitivity to various volatile organiccompounds (VOCs).

Acknowledgement

We thank Department of Physics**,** Faculty of Science in Damascus University for valuable advice and support. This research is financially supported by chemical Department, Faculty of Science in Damascus University and the Higher Institute for Applied Sciences and Technology.

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