Preparation of polyaniline polymer and using it as a vapor sensor of acids

Ashwaq A. Jabor, Karameh A. Mohmmad Ali, Hayder M. Ajeel,

Abdul- Hussain K. Litaif, Resoul H. Mukalaf

Ministry of Science and Technology, IRAQ

E-mail: Ashwak.AlObaidy@yahoo.com

Abstract

Polyaniline organic Semiconductor polymer was prepared by oxidation polymerization by adding hydrochloric acid concentration of 0.1M and potassium per sulfate concentration of 0.2M to 0.1M of aniline at room temperature, the polymer was deposited at glass substrate, the structural and optical properties were studies through UV-VIS, IR, XRD measurements, films have been operated as a sensor of vapor H_2SO_4 and HCl acids.

تحضير بوليمر البولي انيلين وإستخدامه كمتحسس للأبخرة الحامضية

أشواق عبد الحسين جبر، كرامة عبد علي محمد علي، حيدر محمد عجيل،

عبد الحسين خضير الطيف، رسول حسين مخلف

وزارة العلوم والتكنولوجيا، العراق

الخلاصة

تم تحضيرالبولي أنيلين شبه الموصل العضوي ببلمرة التاكسد باضافة حامض الهيروكلوريك بتركيز0.1M والبوتاسيوم بير سلفيات بتركيز 0.2M الى 0.1M من الأنيلين عند درجة حرارة الغرفة رسب البوليمر على قواعد زجاجية ودرست الخواص التركيبية والبصرية من خلال فحوصات XRD و IR و UV-Visb و تم تشغيل اغشية البوليمر كمتحسس لابخرة حوامضH_2SO_4 و HCl .

Introduction

The semiconductor polymers and their derivatives are consider materials which use as sensor since 1980 where were became substitute of metals oxide which works as gases sensors[1,2,3]. Where these polymers characterized that is work at room temperature and high sensitivity in addition have short response time, these polymers have been prepared in many methods such as chemical and electrochemistry techniques, mechanical and electrical properties have been improved through the preparation of polymers derivatives by substitute groups in a polymeric chain. because of unsaturated bonds type π, these polymer behavior as conductor materials, the structure of polyaniline that consist of

benzene ring and electrons non bonds on amine group, these type of semiconductors polymers used as a gas sensor for vapor strong acids such as H_2SO_4, HCL, H_3PO_4, HF, where these type of acids release positive H proton which combine with the non bonds electrons in polymer chain which reduce Conjugated electrons between the series leads to decrement in the electrical conductivity.

Experimental

(1) Preparations of Polyaniline

The polymer was prepared in oxidation polymerization by adding hydrochloric acid concentration (0.1M), aniline solution (0.1M), potassium concentration (0.2 M) and leaves for 24 hours at room temperature where polyaniline consists dark green color, chemical composition is shown in Fig. 1. [4,5].
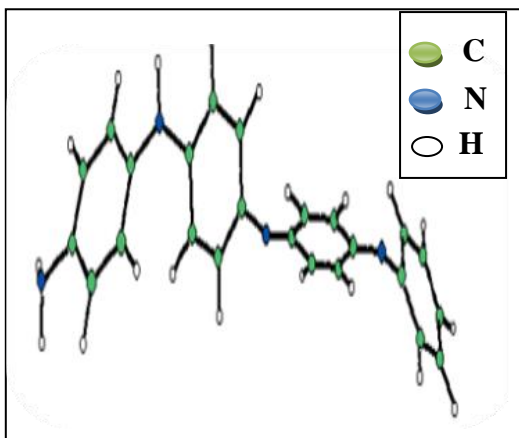

Fig.1: chemical formula of polyaniline.

(2)Preparations of Polyaniline Sensor

Sensor was prepared by deposit aluminum electrode on glass substrate in vacuum evaporation method and that was pouring molten polymer between the electrodes as shown in following Fig. 2. [6,7].
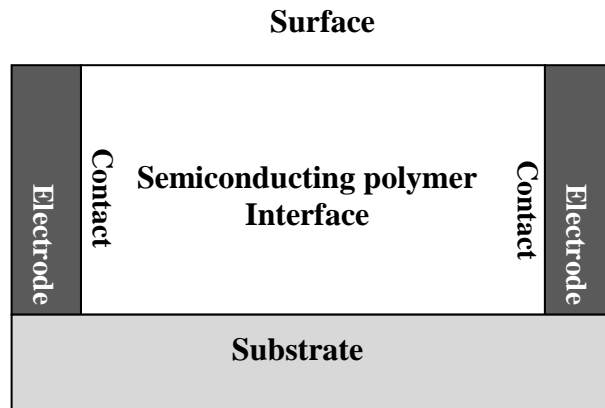
Surface

Fig. 2: sensor design.

Results and Tests

(1)Structural Properties Measurements

A- X-ray tests results

the structure of prepared polymer has been known, It was found a polycrystalline structure, tetragonal type and with common direction (110, 101, 200, 211) as shown in figure below 3 at thickness (800 nm)as well as samples have been tested in (XR - Diffractometer / 6000) Shimadzu model. [4,7].
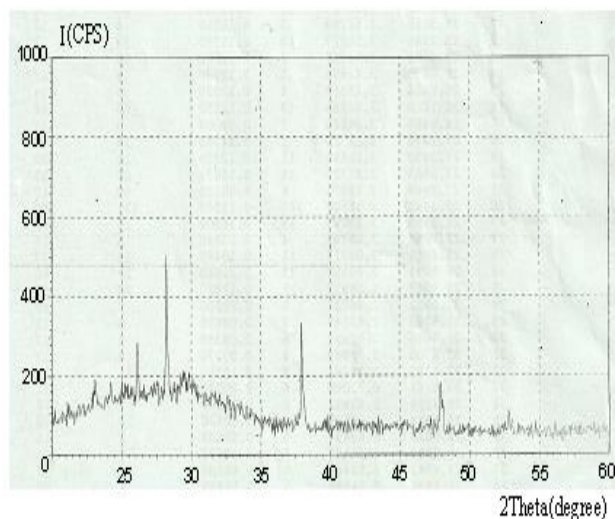

Fig.3: X-ray diffractions of polyaniline thin film.

B- Diagnosis The Prepared Polymer in IR Spectrum[

The Prepared Polymer was diagnosed by using Perkin Elmer FTIR Spectrophotometer model 1720X [8,9].

IR Spectrum of polyaniline

IR Spectral measurements of polyaniline For IR spectrum appeared that there are absorptions bands as shown in the Table 1, Fig.4 illustrates the absorption of IR spectrum.

Tabel 1: The most important absorption bands of the prepared polymer.

| Vibration groups	Absorption bands(cm)$^{-1}$
Stretching vibration (N-H)	2875
Stretching vibration band(C-H)aromatic	3030
Stretching vibration band(C-H) Aliphatic	2850 , 2790
Stretching vibration band (C=C) to the benzene ring	1610 , 1585
Stretching vibration band (C– N)	1328
bending band(C-H) to the benzene ring	1303
Stretching bend N-ph	1029
Stretching band C-H to the benzene ring dual compensation	742
Stretching band C-H to the benzene ring mono compensation	682
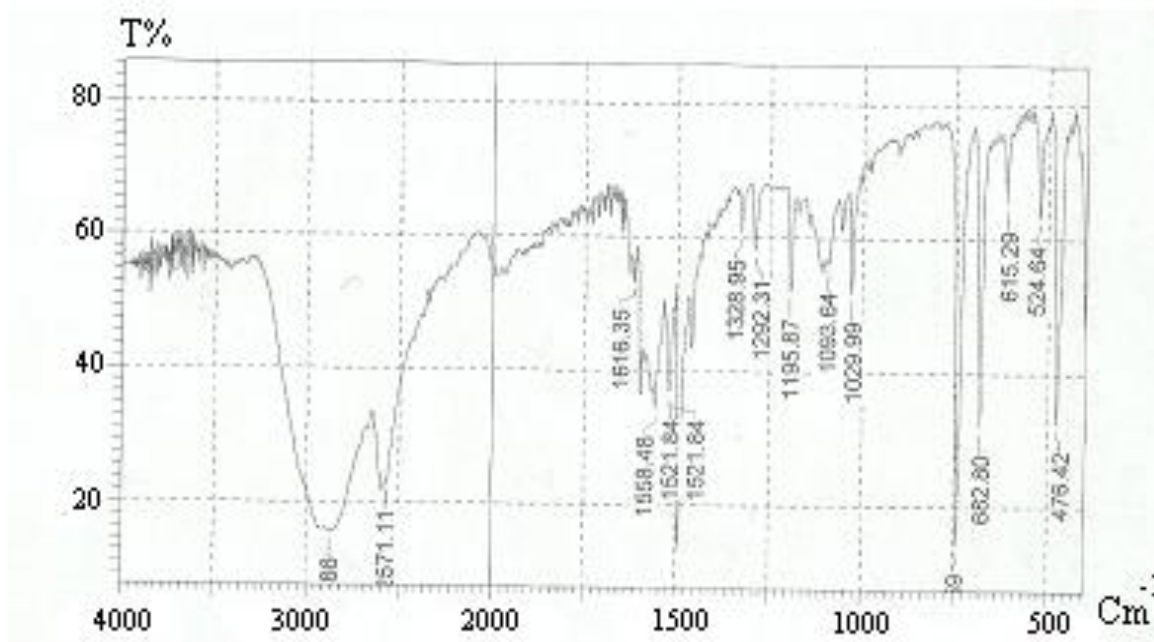
Fig.4: IR spectrum for polyaniline thin film.

(2) Optical Properties Measurements

(2-1)Transmission and Absorption spectrum

Transmission and Absorption measurement were made within spectral range wavelengths (300-800 nm) by using UV-VIS Spectrophotometer/1800 which provides from BIOTECH England company for prepared thin films at thickness of 800 ±5nm at room temperature dissolved in DMF, Fig.5 shows that absorbance values increase at a short wavelengths. [10,11].

(2-2)Absorption Coefficient Calculation
Absorption Coefficient Calculation

Absorption coefficient was calculated as a function of wavelengths for thin films

polymers as shown in Fig.5 The high value of absorption coefficient indicates to the region of curve in which the absorption coefficient change has been slowly in the low energies region (long waves) and the other part of the curve shows that the absorption coefficient increment at high energies region (short waves), from these increment can be determine the principle absorption edge by drawing a tangent to the curve when α =0 and intersection point of X-axis (λ) represents cut off wavelength and its value equal to 480 nm.

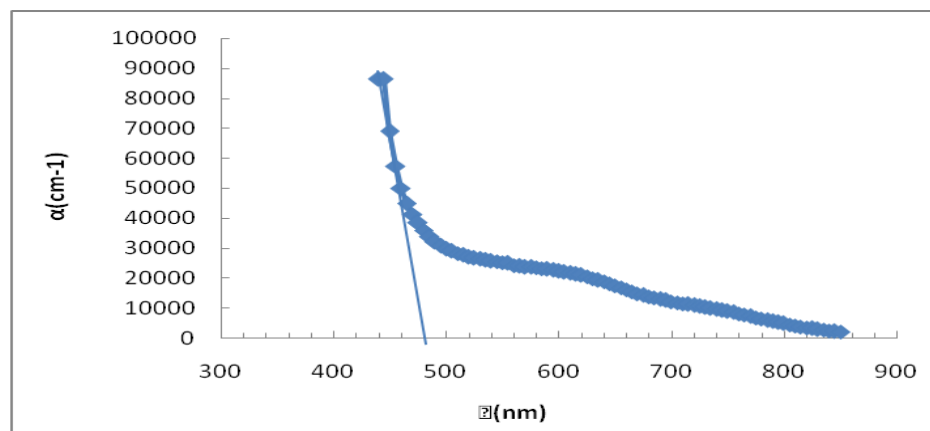**Fig.5: Absorption coefficient as a function of wavelength for polymer thin film at thickness 800 nm.**

(2-3)Sensitivity of thin film Measurements
The following Fig.6 was used to find Sensitivity of thin film for various gases, which consist of the following parts :
1- Vacuum pump (rotary) Manufactured by Edwards company (EDM 12 made in England) to get pressure value $(10^{-2}$mbar).
2- Connecting tubes.

3- Discharge measurement sensor (negative pressure) PRM Manufacture by Edwards.
4- Pressure reader (reader) is manufactured by Edwards.
5- chamber manufactured locally with dimensions (20 x 20) cm that the sample was put in it and several holes including :

A- Hole to pump and discharge gases.
B- Hole use as a glass window.
C- Fead throw to enter and take the signal.
6- D.C Power supply type (DAZHENG).
7- Digital multimeter.
8- Iron stand and holder to formation gas container.

Fig. 6: Gases sensor system.

After connect deposited aluminum electrodes on the film by connected wires, sample is placed on the base inside the chamber, then Gas is pumped, the resistance will be change with the time (per 5 seconds) as well as photoconductivity (I-V) characteristics was measured in case of the gas pump And at the exit of gas to know effect of gas on these thin film. [10,11].

(2-3-1)Sensitivity measurement

Sensitivity can be calculated (S) from equation below:

$$S = (R_g - R_a) / R_a \times 100\% \qquad (2)$$

R_g: The electrical resistance of thin film in the case of the gas pump.

R_a: The electrical resistance of the thin film sensor in the air.

Fig.7 shows the sensitivity of Sulfuric vapor acid and fallow Fig.8 illustrates sensitivity of hydrochloric vapor acid.
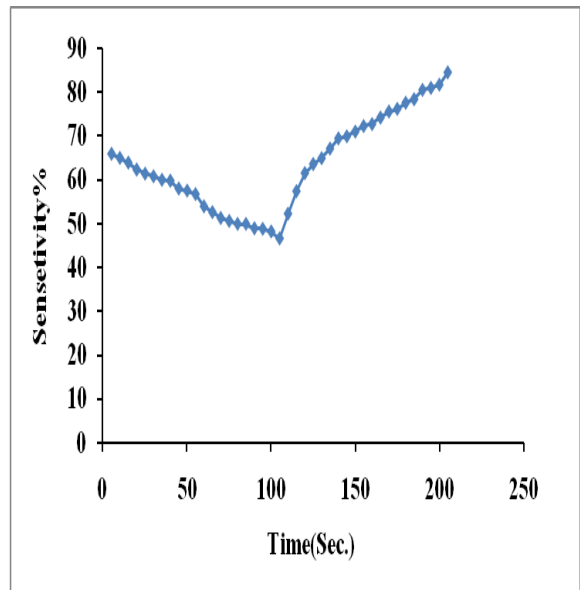

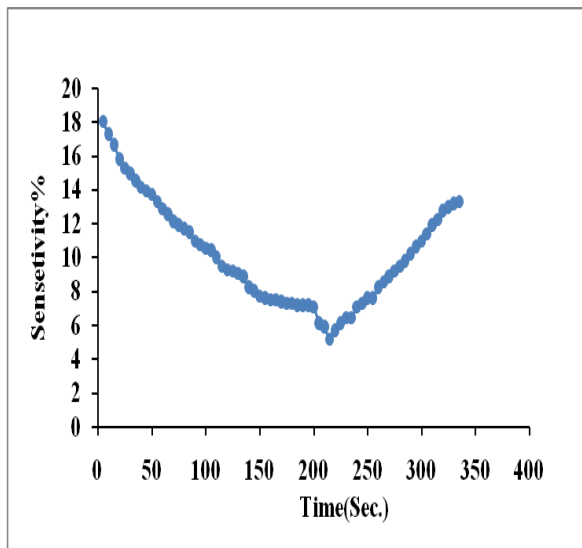*Fig. 7: Sensitivity of Sulfuric acid vapor.*

Fig.8: Sensitivity of hydrochloric acid vapor.

Discussion

Polyaniline appears to be a good candidate to realize gas sensors because of its sensitivity at room temperature, its ease of synthesis by various methods and its low cost. At present, the trend seems to be the use of composite with polyaniline as the sensitive layer. As for the transduction mode, the measurement of dc resistivity variations is the most used technique to monitor the gas adsorption on polyaniline. However, parameters like response time and selectivity of resistive gas sensors remain to be improved.

The measurement of threshold voltage variations, optical or electrochemical parameters under gas flow present several advantages compared to that of resistivity. Polyaniline polymers has been Classified as a good electrical conductivity due to the electronic substituting between amin groups and the benzene ring and the the existence of the electrons mobility and thus become as semiconductor when passes a strong vapor acids on thin film of polymer, that polymer adsorb through Reversible bond of the proton H^+ and amin groups, This bond is reduce from the electrical resistance due to the electron substituting process, these

mechanism is the principle of gases sensor to gas sensing.

Conclusions

1- The results of the XRD analysis show the prepared pure thin films are poly crystalline structure and tetragonal type at thickness (800 nm)± 5nm and the peaks appearance of $2\theta = 26.16$ and $2\theta = 28.244$ due to polyaniline.

2- The results of the spectral analysis of infrared region that the appearance of absorption peaks due to polyaniline chain as well as visible and ultraviolet analysis show high absorbency at the short wavelengths.

3- The results show absorption edge at 480nm.

4- The results of Sensitivity measurements show that polyaniline thin film sensitive to vapor acids of (HCl, H_2So_4).

References

[1] M. Pandey, A. Srivastava, A. Srivastava, R. K. Shukla, Sensors and Transducers, 113 (2010) 33-40.

[2] X. B. Yan, Z. J. Han, Y. Yang, B. K. Tay, Sensors and Actuators B, 123 (2007) 107-113.

[3] D.N.Huyen, In situ chemically polymerized PANi-SWNTs composites: Characterizations and gas sensing feature. Spring. Proc. Phys., 113 (2009) 279-286.

[4] S. Sinha, S. Bhadra, D. Khastgir, J. Appl. Polym. Sci., 112 ,5 (2009) 3135-3140.

[5] C. Dhand, G.Sumana, M. Datta, B. D. Malhotra, Thin Solid Films, 519 (2010) 1145.

[6] G.Bayramoglu, A.Metin, M. Y. Arlca, Appl. Surf. Sci., 256 (2010) 6710.

[7] M. Matsuguchi, T. Yamanaka, M. Yoshida, S. Kojima, S. Okumura, Journal of Electrochemical Society, 156 (2009) 299-302.

[8] P. Chithra lekha, E. Subramanian, D. P. Padiyan, Electrodeposition of polyaniline thin films doped with dodeca tungstophosphoric acid: Effect on annealing

and vapor sensing, Sensors and Actuators B, 122 (2007) 274-281.

[9] S. Virji, R. B. Kaner, B. H. Weiller, Journal of Physical Chemistry B, 110 (2006) 22266-22270.

[10] A. Z. Sadek, W. Wlodarski, K. Kalantar-Zadeh, C. Baker, R. B. Kaner, Sensors and Actuators A, 139 (2007) 53-57.

[11] R. M. G Rajapakshe, A. D. L. Chandani, L. P. P. Lankeshwara, N. L. W. L. Kumarasiri, Synthetic Metals, 83 (1996) 73-76.