INTERNATIONAL JOURNAL OF SCIENCE AND NATURE

www.scienceandnature.org

SYNTHESIS AND CHARACTERIZATION OF POLYPYRROLE AS A GAS SENSOR

[1]Mahdi Hasan Suhail & [2]Ghada Ayad Kadhim
[1]Dept. of physics, college of science, univ. of Baghdad
[2]Dept. of physics, college of science, Univ. of Wassit

ABSTRACT
The composite thin films of polypyrrole (PPy) with functionalized single wall carbon nanotube (fSWCNT) for hydrogen sulfide (H_2S) gas sensing application are presented in this paper. PPy/ fSWCNTs nanocomposite were deposited onto ITO (Indium tin oxide) coated glass substrate by electrochemical polymerization method of pyrrole monomer with oxalic acid and different ratios from functionalized single-walled carbon nanotubes (0.005, 0.01) % in the 150 ml from distilled water. The nanocomposite films were characterized by X-ray diffraction XRD, Fourier Transform Infrared Spectroscopy (FTIR), Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM). The XRD result showed that the deposited films have *polycrystalline* structure at 2θ= (24, 43) ^{o}. The FTIR spectra give distinct and the prominent bonds. The morphological study by AFM showed that formation of uniform granular structure with average grain size of (40.75-47.07) nm. The response of these composite films for H_2S gas was evaluated by monitoring the change in electrical resistance at (20, 50,100,150 and 200) ^{o}C. It is observed that the PPy/ fSWCNT nanocomposite films show a higher sensitivity as compare to pure PPy.

KEYWORDS: electrochemical sensors, H_2S sensor; thin films of polypyrrole (PPy) ,carbon nanotubes (CNTs) , multiwalled carbon nanotubes (MWNT) .

INTRODUCTION

The emission of gaseous pollutants such as sulfur oxide, nitrogen oxide and toxic gases from related industries has become a serious environmental concern. Sensors are needed to detect and measure the concentration of such gaseous pollutants. H_2S is widely used in research laboratories and various chemical industries, and is a very poisonous, corrosive, flammable, and explosive gas with the characteristic foul odor of rotten eggs. An accurate measurement and control of the H_2S gases of low concentrations (exposure to lower concentrations can result in eye irritation, a sore throat and cough) is very important to protect human lives. Materials such as Carbon nanotubes (CNT) and conducting polymers (CP_s) are prime candidates when considering high-strain properties and high-speed response, respectively, as necessary attributes of a composite[1]. The use of fSWCNTs) in biological sensors and effective ultrasensitive chemical because of their high surface-to-volume ratio and their excellent electrical properties[2]. Conducting polymers (CP_s) such as polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy) and their derivatives are widely used in sensing material due to its cost effectiveness, high sensitivity, fast response and room temperature operation[3,4]. Among several conducting polymers, (PPy) and its derivatives have attracted a great deal of attention because of its high electrical conductivity, good environmental stability and simple synthesis and processing. Furthermore, PPy is among a small number of materials demonstrating gas sensing features at room temperature, a fascinating prospect for developing practical applications [5-7].

The polypyrrole consists of a 5-membered ring, containing a nitrogen (N) heteroatom, the same as with otherorganic molecules, PPy polymerisation occurs upon oxidation of the monomer, which forms a CP backbone chain with overlapping pi-orbitals and a positive charge along the polymer backbone[8]. PPy backbone chain has an alternating single and double bond. Fig. (1) shows the molecular structure of polypyrrole.

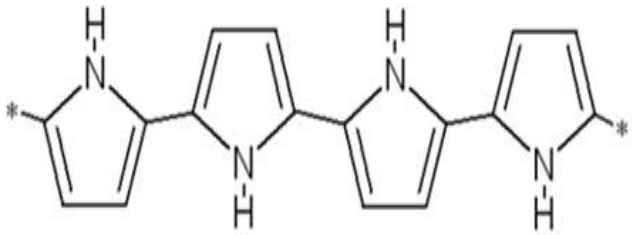

FIGURE 1: Structure of polypyrrole in the netural state

The electrochemical approach for making electroactive/ conductive films is very versatile and provides a facile way to vary the film properties by simply varying the electrolysis conditions (*e.g.* electrode potential, current density, solvent, and electrolyte) in a controlled way. Furthermore, the electrosynthesis allows an easy control of the thickness of the polymers. The nature and concentration of monomer/electrolyte, cell conditions, the solvent, electrode, applied potential and temperature, pH all have a strong effect on the electro-oxidation reaction and the quality of the film [9-11]. In this study, the characterizations of structural and morphology properties for PPy/fSWCNT nanocomposite thin films were investigated. The films were study for 30% pmm H_2S gas at various temperature (20, 50,100,150 and 200)^oC

Experimental

PPy/fSWCNTs films was prepared from pyrrole (Py) monomer in acid medium at room temperature by used ITO as a reference electrode and titanium as working electrode. Substrate of ITO has been chemically and ultrasonically cleaned by typical methods. PPy solution is prepared by using 0.1M of pyrrole monomer was doping with oxalic acid (0.1M) with different concentration from (fSWCNT) (0.005 and 0.01) % in 150 ml from distilled water . The synthesized electrodes were thoroughly washed with water to avert the possible presence of electrolyte species on the surface of polymer nanocomposite films were deposited at (4.9 and 4.7) V with different ratio of CNT wthin 3 minutes. The prepared thin film was uniform, green and strongly adherent to substrate. The thickness of the nanocomposite was100nm measured using an optical interferometer by using He-Ne laser (0.632µm). Mask on the films surface from Aluminum of 100 nm thickness was deposited using thermal evaporation. The characterizations of structural properties for nanocomposite thin films were investigated by X-ray diffractometer (Shimadza-6000) using CuK_α radiation. The morphology of the nanocomposite thin films was studied using atomic force microscope (Angstrom, AA3000), Fourier Transform Infrared Spectroscopy was studied by using solid KBr discs Maximum Resolution 0.5cm and the microstructure film study by Hitachi FE-SEM model S-4160. 30 % ppm from $H_2S$was introduced to the chamber at various temperature (20, 50,100,150,200) ^oC.

RESULTS & DISCUSSION

XRD Analysis

The structural characteristics of the PPy and PPy/fSWCNT films have been analyzed by X-ray diffraction pattern as shown in Fig. 2.

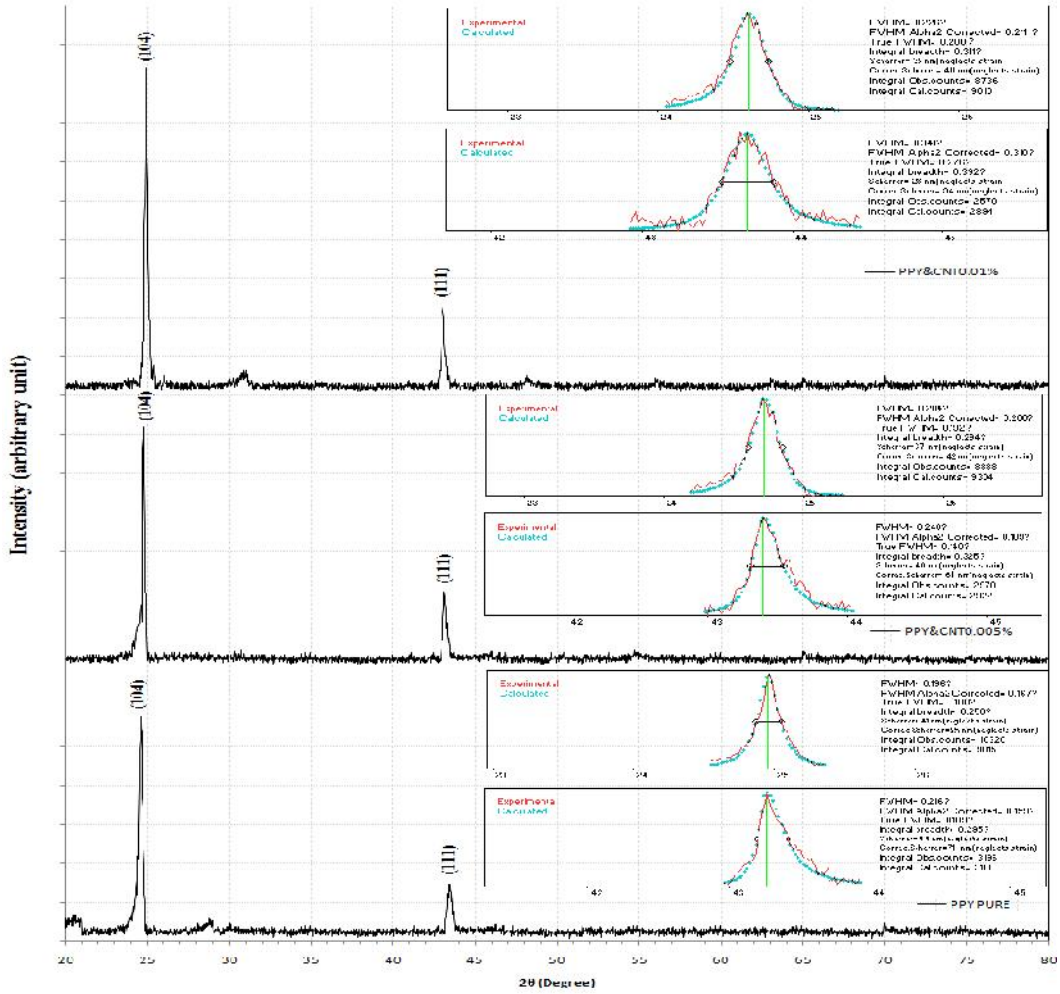

FIGURE 2. XRD pattern of PPy and (PPy/SWNT) films

Diffraction pattern of films has *Polycrystalline* structure at diffraction angles 2θ=24,43° which is a characteristic peaks of (PPy/fSWCNTs)[13,14]. The peaks become sharp and increase in intensity with increasing the concentration of (fSWCNT) and have different average grain size which is calculated by using Debye – Scherer equation.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{…. (1)}$$

where k is shape factor for average crystallite, β is full width at half maxima (FWHM) of crystalline planes in radians, θ is the angle between incident and reflected rays and λ is the wavelength of the X-ray which is 1.54Å for Cu target. The average grain size increase with increasing concentration of fSWCNT.

AFM Analysis

The morphology of films was examined using an (AFM). Fig. (3) Shows the 3D AFM images of the PPy and (PPy/fSWCNT) films.

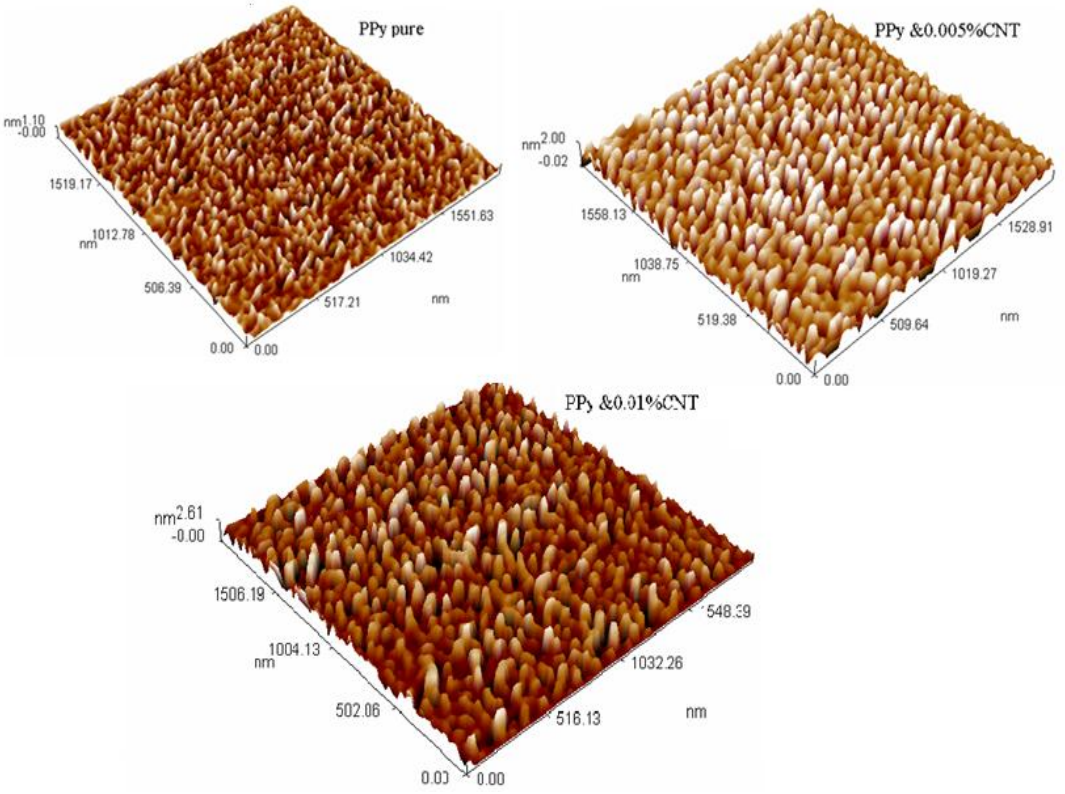

FIGURE 3. 3-D AFM image of nanostructured PPy and (PPy/fSWCNT) films

AFM results showed homogenous, smooth nanocomposite films and have different average grain size with various concentrations from fSWCNT. The increase of the crystallite size may be caused by columnar grain growth in the structure through increasing concentration of fSWCNT. The results of crystallite size obtained from XRD are in good agreement with those obtained from AFM shown in Table.1.

TABLE 1: Values of the grain size (GS) calculated from XRD and AFM investigations

Sample	2θ (Deg.)	GS (XRD measurement) nm	Average GS (AFM investigation) nm
Pure PPy	24.6	36.0	40.75
	43.0	25.1	
PPy&CNT 0.005%	24.8	39.9	44.81
	43.12	35.6	
PPy& CNT 0.01%	24.92	41.5	45.15
	43.0	39.5	

FTIR Analysis

The chemical structures of nanocomposite thin films were determined by FTIR Spectroscopy. The FTIR spectra of PPy and PPy/fSWCNTs at (0.005 and 0.01) % from fSWCNTs are shown in Fig. 4.

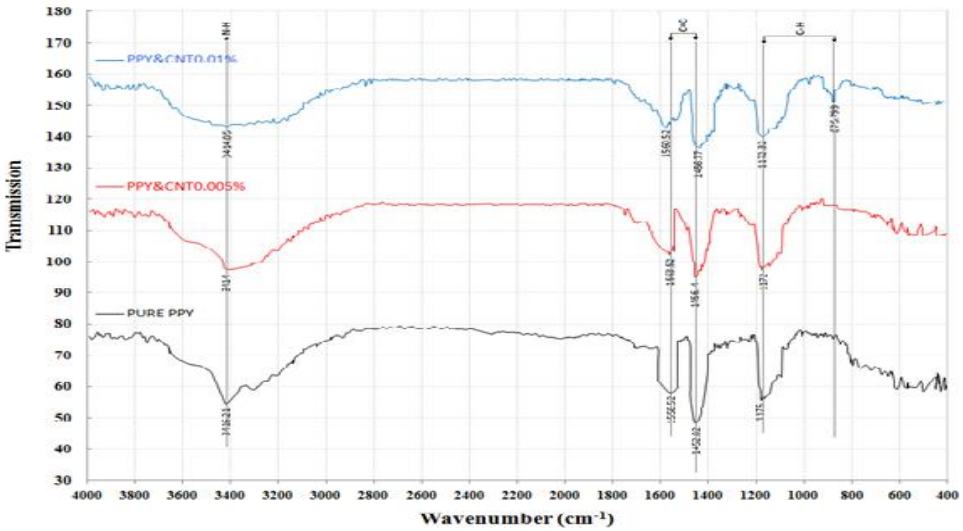

Figure4. FTIR spectra of the PPy and PPy/fSWCNT films

In the spectra of Pure PPy, a broad absorption band obtained a stretching N-H band at 3416.21 cm^{-1}. The bands at (1558.52 and 1452.82) cm^{-1} is related to the C=Cstretching mode, and the bands at 1176 cm^{-1} is associated to the C-H bending modes while the band for C-H out-of-plane deformation vibration was observed at 875.799 cm^{-1}after add 0.01% fSWCNT, After addition we note a slight change in bonds values and a decrease in intensity and this is attributed to the presence of fSWCNT, which are coincident with the literature [6, 11] as shown in Table 2.

TABLE 2: shows the value of bonds for PPy/fSWCNT nanocomposite films through a FTIR analysis

Sample	N-H	C=C	C-H
Pure PPy	3416.21	1558.52	1176
		1452.82	
PPy & CNT 0.005%	3414	1563.52	1172
		1456.4	
PPy & CNT0.01%	3414.85	1560.52	1172.32
		1456.77	875.799

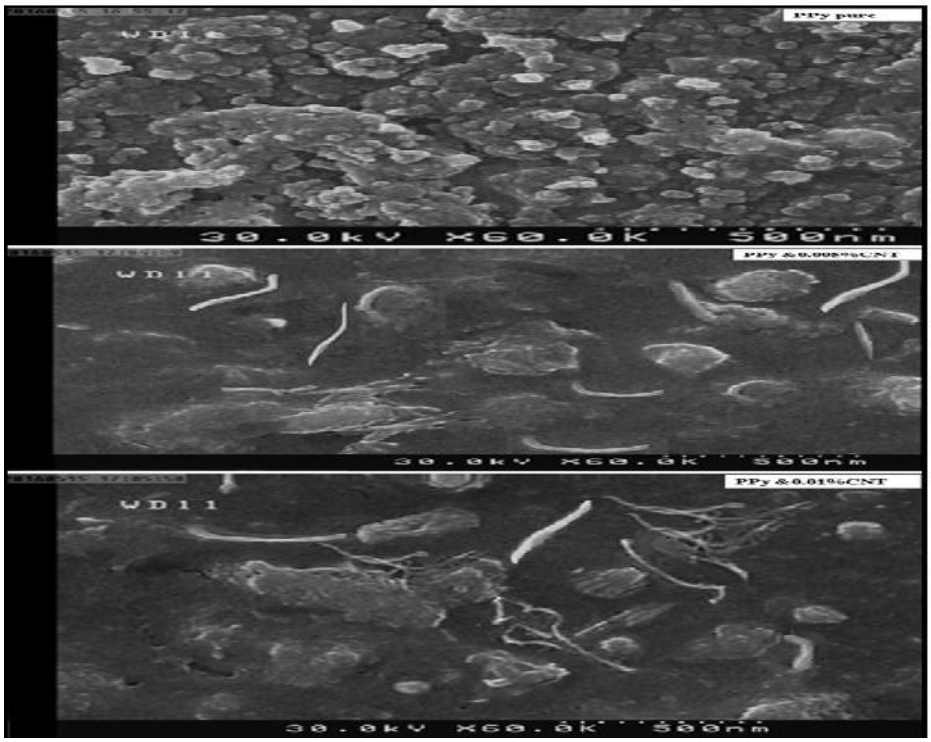

FIGURE 5. FESEM images of PPy and PPy/f SWCNTs, scale bar 500 nm

SEM analysis

The Scanning Electron Microscopy (SEM) images of pure PPy and PPy/fSWCNT nanocomposites are shown in Fig. 5. It can be observed the pure PPy has granular structure with particle size in the range (36-75) nm, but in the nanocomposite films resulting in spherical and cylindrical forms. The spherical structures are believed to arise from PPy without CNT while the cylindrical forms refer to the fSWCNT.

Hall measurements

Hall coefficient, the type of charge carriers, conductivity, concentration (n_H) and Hall mobility (μ_H) have been estimated from Hall measurements for pure PPy and (PPy/ fSWCNT) films were deposited on (ITO) glass substrates. The values of carrier concentration (n_H) and Hall mobility (μ_H) were calculated using equations[12].

$$RH = \frac{1}{p.q} \quad \ldots . (2)$$

$$\mu_H = \sigma |R_H| \quad \ldots . (3)$$

Where p is the type of charge carrier and q is the charge of electron.

The type of charge carriers is p-type for all pure PPy and PPy/ fSWCNT films. The variation of carriers concentration (n_H) and Hall mobility (μ_H) of thin films are shown in Table (3).

TABLE 3: shows conductivity, Hall coefficient, concentration (n_H) and Hall mobility (μ_H)

CN/PPy	σ_{RT} ($\Omega^{-1}.cm^{-1}$) x10^3	R_H	n_H (cm^{-3})x10^{19}	μ_H (cm^2/v.sec)
0.0	0.532	0.03435	18.2	18.29
0.005	0.946	0.03765	16.6	35.60
0.010	2.17	0.02	31.3	43.30

Sensor measurements

The substrate is coated with 100 nm thick PPy and (PPy /fSWNT) layer. The electrode is made by depositing aluminum on the film with 100 nm thickness. Gas sensing measured from the variation of resistance with the time at five different temperatures (20, 50,100,150 and 200) ^oC at 30% from (H_2S). Figs. (6-8) show the Variation of resistance with time to pure PPy and PPy/fSWCNT with (0.005and 0.01) %CNT respectively at different operation temperature.

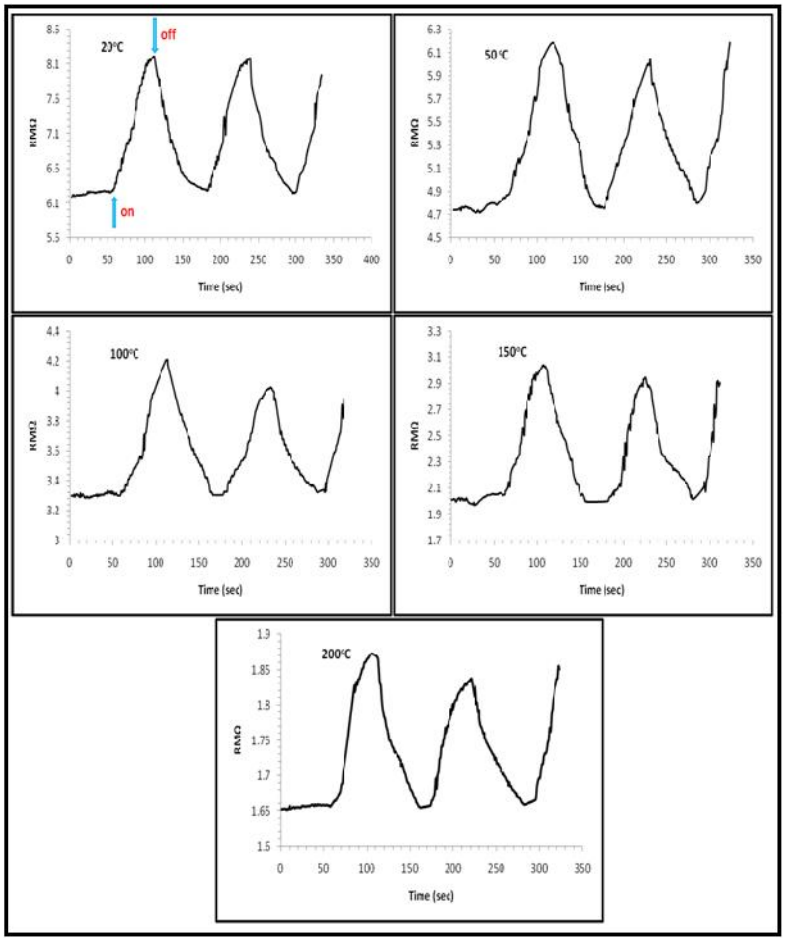

FIGURE 6: The Variation of resistance with time to pure PPy at different operation temperature

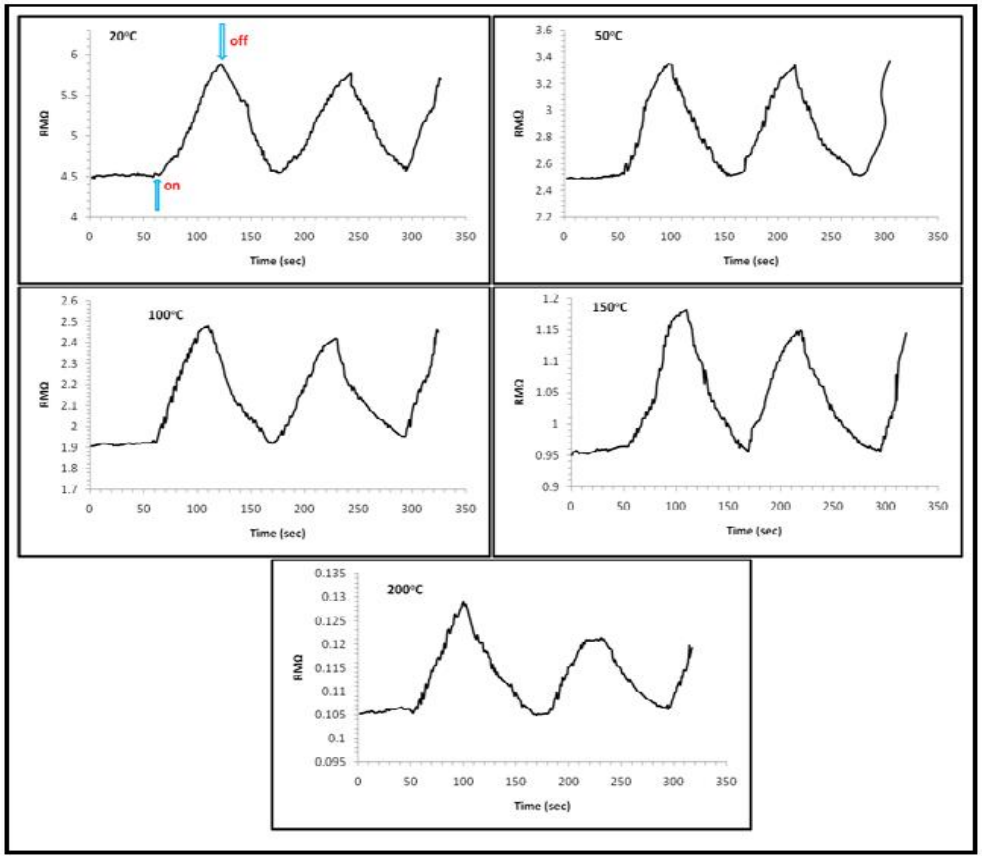

FIGURE 7: The Variation of resistance with time to PPy and 0.005%fSWCNT at different operation temperature

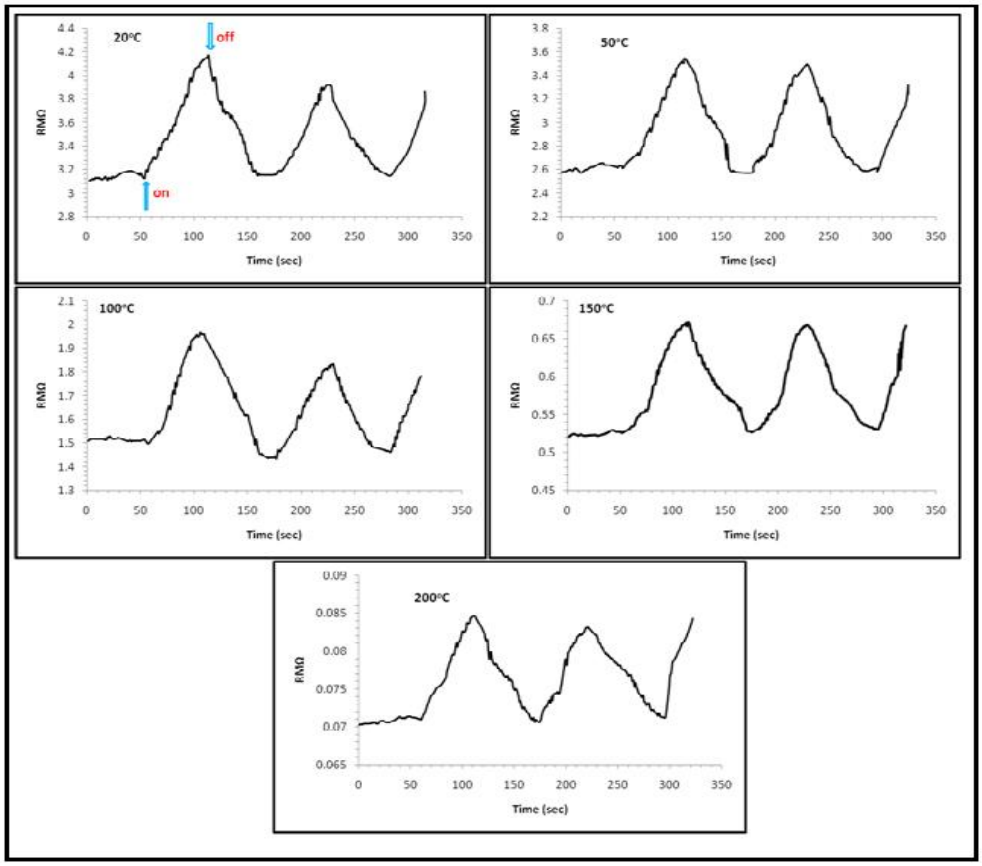

FIGURE 8: The Variation of resistance with time to PPy and 0.01%fSWCNT) at different operation temperature

The resistance increases in opened gas case and decreases rapidly in closed gas the reason for this behavior can be attributed to the following: The sensing mechanism of PPy and PPy /fSWNT gas sensors can be explained by the adsorption of oxygen on the surface of film grains and its reaction with H_2S gas molecules. By introducing H_2S gas molecules, the electrical conductivity of film changes due to the surface reactions at the grains. Reaction of these adsorbed oxygen ions with H_2S gas causes a decrease in band bending and changes the conductivity of grain. The H^+ reacts with adsorbed oxygen ions and form water vapor, and as a result of this reaction, electron transfer back to the film according to the reaction [13]. The transfer of electrons to the conduction band in p-type makes the semiconductor less p -type, and the film resistance increases. Fig. (9) shows the variation of the sensitivity of the tested films as a function of temperature. It can be observed that the sensitivity increases as the temperature increases from room temperature to 50°C. Over 50°C, sensor sensitivity decreases with the increasing temperature. The sensitivity increasing at increase the concentration of SWCNT, The best sensitivity of the samples found at 50°C because 50°C suitable for vibration of atoms and moving charge carriers to meet the requirements of the sensor where the material acquires this energy and become charges more free.

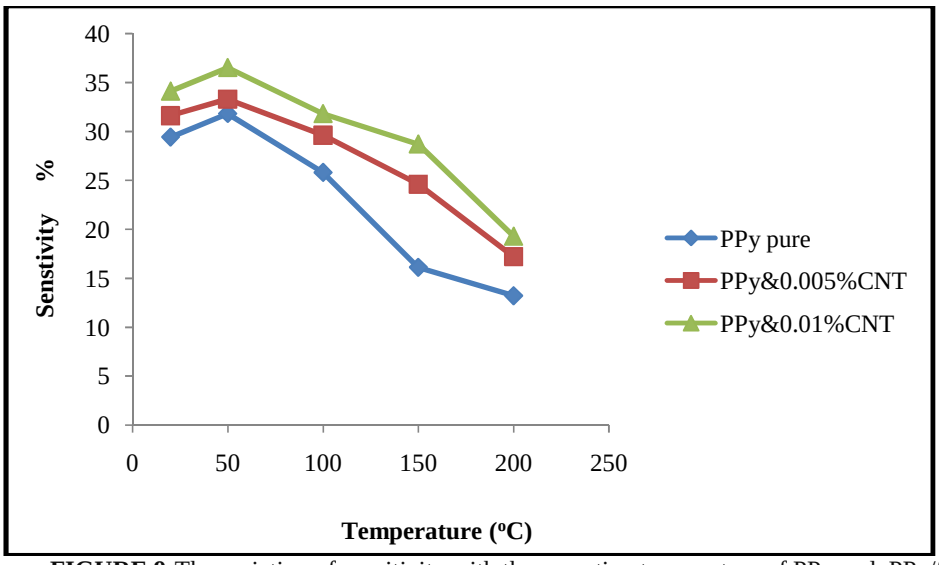

FIGURE 9: The variation of sensitivity with the operating temperature of PPy and PPy/fSWCNT films

Figs. (10, 11) shows the variation of Response time and recovery time respectively with operating temperature of PPy and PPy/fSWCNT films.

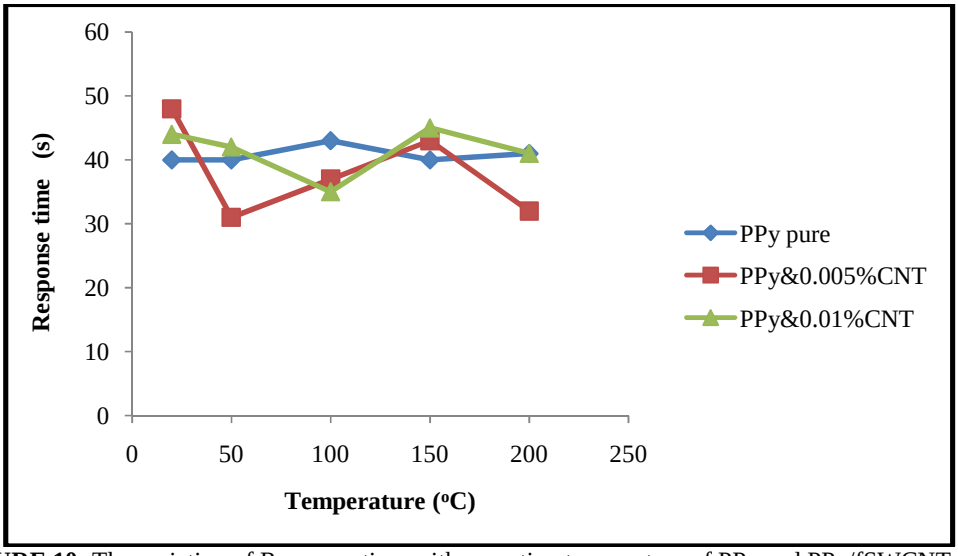

FIGURE 10: The variation of Response time with operating temperature of PPy and PPy/fSWCNT films

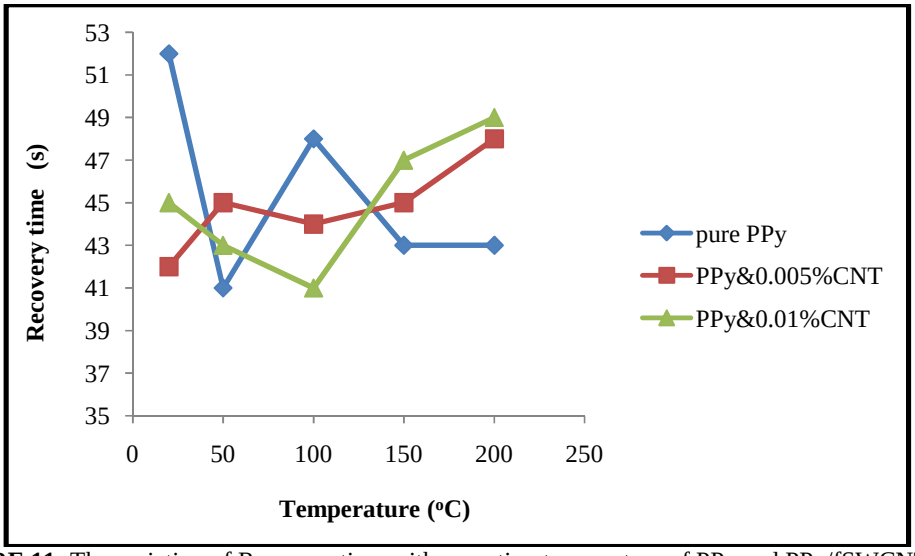

FIGURE 11: The variation of Recovery time with operating temperature of PPy and PPy/fSWCNT films

CONCLUSION

In concluding remarks, we have synthesized PPy and PPy/ fSWCNT by electrochemical polymerization method. XRD studies revealed that thin films are polycrystalline. it show an increase in grain size with increase the concentration of CNT and observed the less aggregation of the polymer from AFM. Proper formation of the PPy and PPy/ fSWCNT films in a conducting form was established by FTIR measurement. Gas sensing characteristics shows response for H_2S gas with operated temperature 50^{o}C.

REFERENCES

[1]. Dos Santos, M.R. & De Oliveira, H. P. (2014) Simple method for mass production of polypyrrole /carbon nanotubes hybrid artificial muscle. Quim. Nova, 37(6), 1000-1003.

[2]. Hong, J., Phiboolsirichit, N., Mubeen, S., Deshusses, M., Mulchandani, A. & Myung, N. (2010) Electrical and gas sensing properties of polyaniline functionalized single-walled carbon nanotubes. Nanotechnology 2, 1-7.

[3]. Kondawar, S.B., Patil, S.B. and Agrawal, S.P. (2014) Chemical Vapour Sensing Properties of Electrospun Nanofibers of Polyaniline/ZnO Nanocomposites. Advanced Material Letters, 5(7), 389-395.

[4]. Bachhav, S.G. and Patil, D.R. (2015) Study of Polypyrrole-Coated MWCNT Nanocomposites for Ammonia Sensing at Room Temperature, Journal of Materials Science and Chemical Engineering. 3, 30-44.

[5]. Whitby, R.L., Korobeinyk, A., Mikhalovsky, S.V., Fukuda T. and Maekawa, T. (2011) Morphological Effects of Single-Layer Graphene Oxide in the Formation of Covalently Bonded Polypyrrole Composites Using Intermediate Diisocyanate Chemistry. Journal of Nanoparticle Research.13, 4829-4837.

[6]. Sirivisoot, S., Pareta, R. and Webster, T.J. (2011) Electrically Controlled Drug Release from Nanostructured Polypyrrole Coated on Titanium, Nanotechnology, 22(8), Article ID: 085101.

[7]. Ram, M.K., Bhethanabotla, V.R. (2010) Sensors for Chemical and Biological Applications, CRC Press: Boca Raton, FL, USA.

[8]. Hamilton, A. (2012) The Formation and Characterisation of a Polypyrrole Based Sensor for the Detection of Urea. National University of reland Maynooth.

[9]. Bradner F.P. and Shapiro, J.S. (1988) Improvement in the quality of polypyrrole films prepared electro chemically on a mercury anode/ Synthetic Metals/ 26, 69-77.

[10]. Stradiotto, N.R., Yamanaka, H., Valnice M. and Zanoni, B. (2003) electrochemical sensors: A powerful tool in analytical chemistry. J. Braz. Chem. Soc., 14 (2), 159-173.

[11]. Mohammed, R.A. (2014) an investigation of electro polymerization and corrosion protection properties of polypyrrole coating on carbon steel and stainless steel. Scientific Research University of Baghdad.

[12]. Meyyappan, M. (2004) Carbon nanotubes: Science and Applications (CRC Press, Boco Raton, Fla, USA.

[13]. Cappus, D., HaBel, M., Neuhaus, E., Heber, M., Rohrand, F., Freund, H. (1995) Polar surfaces of oxides: reactivity and reconstruction Surface Science. 337: 268-277.