

Effect The Finalizations Multi Wall Carbon Nanotube on The Characteristics of Polypyrrole Thin Films

Ghada A. Kadhim¹, Walaa M. Aliradha² and Amer A. Ramadhan³

¹Department of Physics, College of Science, University of Wassit, Iraq

²Ministry of education, The General Directorate For education of Diyala

³Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Abstract

The nanocomposite (PPy/fMWCNT) is prepared via electrochemical polymerization onto indium tin oxide (ITO) coated glass for pyrrole (Py) monomer with oxalic acid ($C_2H_2O_4$) and various concentration from functionalized multi wall carbon nanotube fMWCNT (0.01, 0.02) in the 130 mL from distilled water. The structure, morphology and optical properties of thin films were investigated via X-Ray diffraction (XRD), Field Emission Scanning Electron microscopy (FE-SEM), ultraviolet-visible (UV-VIS) spectroscopy and Fourier Transform Infrared (FT-IR) Spectroscopy. The X-ray diffraction pattern indicates that the prepared thin films are of polycrystalline structure at $2\theta = (25, 42)^\circ$. The band gap of thin films decreases from 2.4 to 2.09 eV as the fMWCNT increased from 0.01 to 0.02 M, whereas FTIR showing the distinctive bonds of these films.

1. Introduction

Conductive polymers (CPs) have been studied over the past two decade [1]. CPs such as polyaniline (PANI), polythiophene (PTH) and polypyrrole (ppy). CPs have π -electron backbone which is responsible for their uncommon electronic properties like low energy optical transition, electrical conductivity, high electron affinity

and low ionization potential. And are used to enhance speed, sensitivity and versatility of sensors. CPs properties depend strongly on ion size of the dopant, doping level, water content and protonation level. CPs finding ever-increasing use in diagnostic medical reagents and with a recognizable chemical memory are prominent novel materials for the fabrication of industrial sensors [2, 3]. Simple CPs moreover show exciting

physicochemical properties that are potentially useful to sensors, batteries, electrochromic displays, light emitting diodes, etc. [4, 5]. polypyrrole is one of the most important CPs and is a promising CPs for commercial applications, environmental stability, good and ease of synthesis and owing to its high conductivity. On the other hand, PPy is infusible and insoluble, which restricts its fabrication and it, has poor mechanical properties. One of the ways to avert these problems is to use an electrically conductive tissue composite, since this not only has the resiliency of a tissue and flexibility and excellent mechanical strength, however too retains the electrical properties of the CP [6]. Carbon nanotubes (CNTs) have attracted considerable attention for the construction of nano and micro-devices since the finding of CNTs by Iijima in 1991 [7]. CNTs are distinctive nanostructured materials with significant mechanical properties and physical [8]. With their mechanical strength, high electronic conductivity, surface area and aspect ratio, CNTs have aroused considerable importance in electrochemical applications as actuators and sensor electrodes and capacitor [9, 10]. Several studies have

focused on pure carbon nanotube assemblies, for example, for use in double-layer capacitors, while others have extended to combinations together with conducting polymers [9, 11]. The desired merging of CNT and conducting polymer properties in composite form presents new opportunities to produce superior materials for applications like electrochemical capacitors, actuators and sensors. To date, most reports on electrochemically grown MWNT-CP films have focused on those based on PPy since this conducting polymer offers a greater degree of electrochemical processing flexibility than most other commercially available CPs [12, 13]. Composite materials of CNTs and polymers have attracted great interest because they may possess novel combinations with superior characteristics than either of the individual components [14]. Electropolymerization of CPs has been proven to be a good technique for the deposition and synthesis of such CPs, allowing the production of polymer coatings with high levels of conductivity and chemical stability [15]. This method is, however, largely limited to conductive substrates. Although some specially manufactured or modified ICPs can

be dissolved in solvents, [16] most of them are intractable and insoluble in common organic solvents in their original form; therefore, preparation of the desired composite structures is a time-consuming process and requires a series of different steps and components. Because of this technological barrier, some research groups have tried to use electrodeless methods for the deposition of conductive polymers on diverse substrates. [17,18] But there has been some success in forming thin films of conductive polymers over surfaces using such techniques, the slow rates of polymerization and unavoidable polymerization in the solution make these methods inefficient [19]. The electrochemical growth of MWNT-CP composites offers the ability to produce three dimensional nanostructured thin films that combine the redox pseudo-capacitive charge storage mechanism of conducting polymers with the high surface area and conductivity of MWNTs [20]. The electrochemical synthesis is more exciting than the chemical one in the sense that it offers control of the polymerization and doping level, and could be produced over a number of substrates in order to fabricate devices directly. When

using electrochemical methods, these polymers can be synthesized by anodic oxidation of the consistent monomers in suitable electrolytes. In addition, the nature and the size of the counter-ions used have a great effect on the physical properties of the polymer coatings (porosity, morphology, thermal stability and mechanical properties) [21].

2. Experimental

PPy and fMWCNT nanocomposites were synthesis from pyrrole (Py) monomer in acid medium at room temperature by used titanium as working electrode and Indium tin oxide as a reference electrode. ITO has been chemically and ultrasonically cleaned by typical methods. solution of PPy is prepared via using 0.2M of Py monomer was doping with oxalic acid (0.2M) with various concentration of (fMWCNT) (0.01 and 0.02) in 130 ML from distilled water. The synthesized electrodes were thoroughly washed by water to evade the possible presence of electrolyte species on the surface of polymer. PPy/fMWCNT thin films were deposited at (4.9 and 4) V with various concentration of fMWCNT within 3 minutes. The prepared thin

film was identical, green, and strongly adherent to ITO substrate. The thickness of the thin films was 105nm measured using an optical interferometer via using He-Ne laser (0.632 μ m. The characterization of structural properties for samples was investigated via X-ray diffractometer (XRD, Shimadza-6000) using CuK α radiation, the microstructure film study via Hitachi FE-SEM model S-4160. Optical properties studied by ultraviolet-visible (UV-VIS) spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR) was studied by using solid KBr discs Maximum Resolution 0.5cm.

3. Result and discussion

3.1. XRD Analysis

Figure (1) show analyze the structural characteristics of the pure PPy and PPy/fMWCNTs films via X-ray diffraction. Diffraction pattern of film has Polycrystalline structure at $2\theta=25,42^\circ$ which is a distinguishing peaks of (PPy/fMWCNTs) this corresponds with [22]. The peaks increase in intensity and become sharp with increasing the ratios of fMWCNT this lead to increase crystal size calculated by using Debye – Scherer equation.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where λ is the wavelength of the X-ray which is 1.54 $\text{\AA}$ for Cu target, k is shape factor for average crystallite, β is full width at half maxima (FWHM) of crystalline planes, θ is the angle between incident and reflected rays.

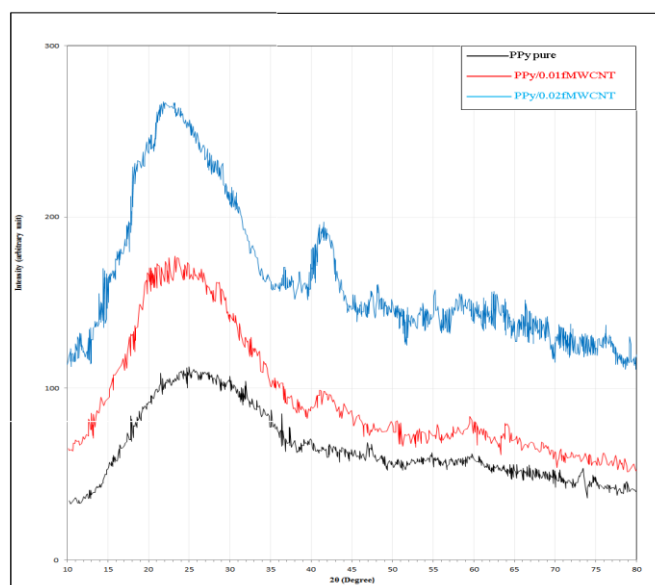
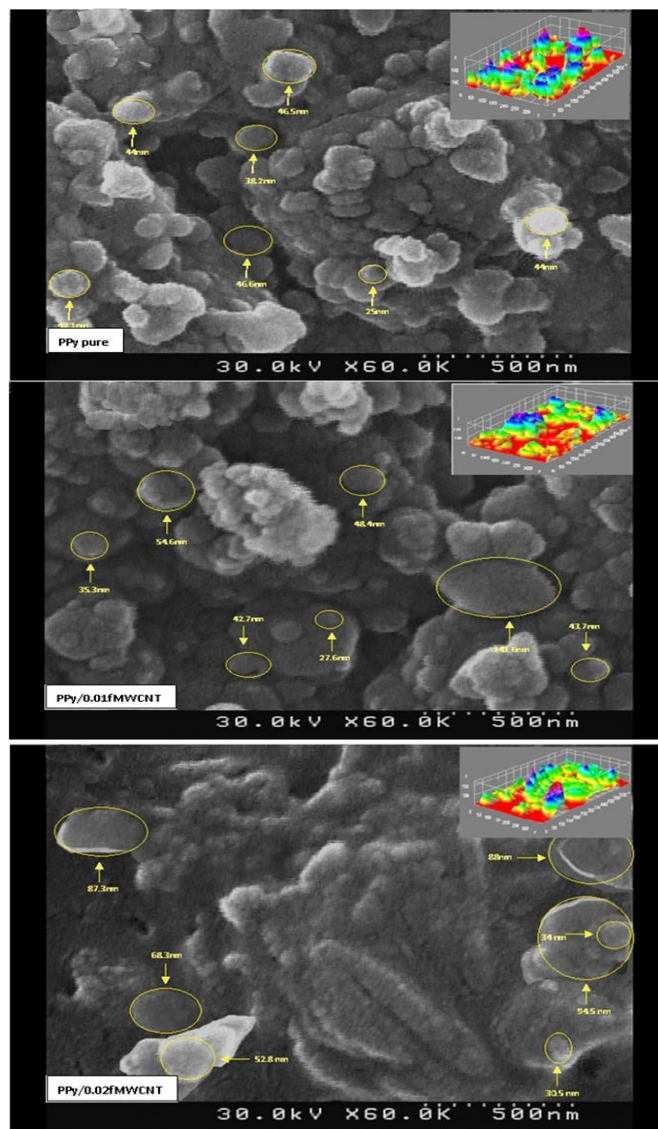


Fig. (1). XRD pattern of PPy and (PPy/fMWCNT) thin films

3.2. SEM analysis

The Field Emission Scanning Electron Microscopy (FE-SEM) images of pure PPy, and PPy/fMWCNT film using different concentrations of fMWCNTs suspended in the polymerization electrolyte on ITO substrate interactive 3D surface of films at the operating voltage of 30kV and 60,000 times magnification are shown in

figure(2). the pure PPy has a granular structure with a verage grain size 39.74nm, but in the nanocomposite we can be observed that many nanotubes with number of granular because presence of CNTs. Increasing the concentration of CNTs lead to increase the average grain size as well as increase of nanotubs [23] .



(PPy/f MWCNTs), scale bar 500 nm.

3.3. (UV-VIS) spectroscopy analysis

The characteristics of the absorption can be considered as a useful tool to analyze nanomaterials. It is obviously seen that the absorption is decreasing sharply below 300nm. The 300 nm adsorption band represents the π^* - π transition. As can be seen from figure (3), the absorption increases with increasing the concentration of CNT. The change in the intensity of absorption indicates a modification in electronic structure and a relocation of polaron levels in polypyrrole band gap due to the interaction with MWCNTs. The figure has three curves, each curve has one regions in UV range has a maximum value (2.6 to 3.6) % of absorbance, precisely at 300 nm.

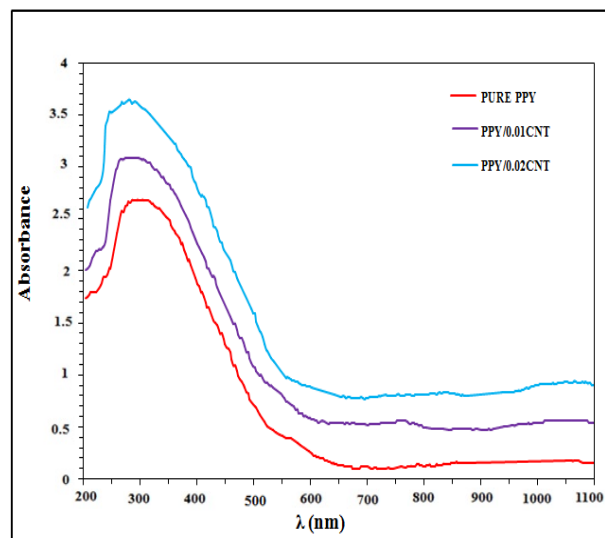


Fig. (3): Optical absorbance for PPy and (PPy/MCNT) thin films.

Figure (4) shows the optical transmittance of of PPy and

PPy/MWCNT thin films deposited on ITO glass with diverse concentration from fMWCNTs as a function of the wavelength range (200-1100) nm. From the figure, we observe three curves, each curve has two areas. The first one in UV range has a value (12 to 32)% of transmittance, exactly at 200 nm, also, the second region from the range (550-1100)nm, in this region we can see that increase of the transmittance to (56 to 90)%. Also, the transmittance decreases with the increase in the concentration of fMWCNT.

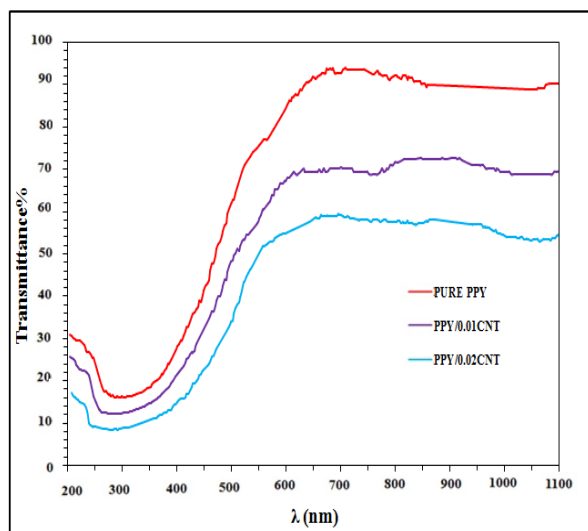


Fig. (4): Optical transmittance for PPy and (PPy/SWCNT) thin films.

Figure (5) Displays the plot of $(\alpha h\nu)^2$ versus $h\nu$ for PPy and (fMWCNT) films. It can be seen from this figure that the transition is direct transition, energy gap (E_g) decreases

with increase the fMWCNT as shown from Table (1) this result can be ascribed to the increasing crystallite size with the increase of fMWCNT concentration. The value of band gap of the thin films is due to quantum size effect.

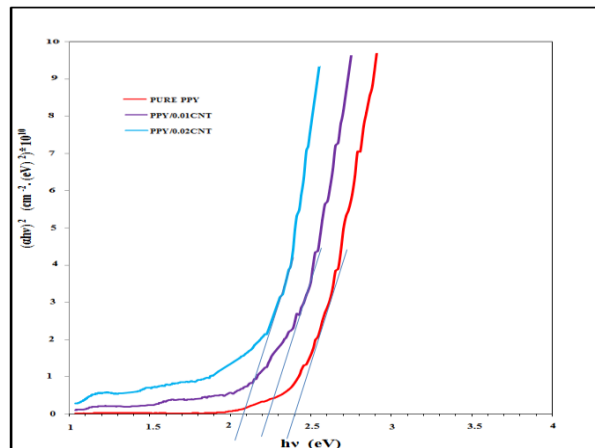


Fig. (5): Show relation between $(\alpha h\nu)^2$ and photon energy ($h\nu$) for PPy and (PPy/fMWCNT) thin films.

Table 1: The energy gap values of thin films with the different concentration of fMWCNT

Sample	Energy gap (eV)
Pure PPy	2.4
PPy/0.01CNT	2.23
PPy /0.02CNT	2.09

3.4. FTIR analysis

The FT-IR spectra recorded for PPy and PPy/fMWCNT nanocomposites with different ratio from fMWCNT deposited on ITO

glass substrate are shown in figure (6). In the spectra of Pure PPy, the absorption bands double bonds C=C obtained at 1650 cm^{-1} is likely the most affected PPy sites in the nanocomposite and 1400 cm^{-1} corresponds to symmetrical C-C stretching vibration in pyrrole ring. The double bonds C=N at 1230 cm^{-1} is associated the ring deformation, while the band for C-H out of plane deformation vibration was observed at $(1000\text{ and }880)\text{ cm}^{-1}$ [24]. It was observed that all the spectra contain a very weak but broad adsorption band in the region between 2500 cm^{-1} to 3500 cm^{-1} , which is commonly assigned for the adsorption band of O-H, C-H, N-H groups [25]. The characteristic peaks of PPy at 1400 cm^{-1} is also observed for the PPy/fMWCNT nanocomposites, indicating the formation of PPy in the presence of fMWCNT. It is important to observe that peak of PPy at 1657 cm^{-1} becomes slightly broaden in almost all nanocomposite samples and we see the better interaction between the aromatic ring of pyrrole and fMWCNT. It is observed that all the peaks appeared in the fingerprint region of PPy are observed in the FTIR spectra of PPy/fMWCNT nanocomposites indicating the main constituents of PPy and its

nanocomposite with fMWCNTs have the same chemical structure. However, the incorporation of MWCNT results into the slight shifting of FTIR bands from its original position. This shift in peak position is due to the strong interaction, loss in conjugation and molecular order after modification of PPy with fMWCNTs and can be attributed to the chemical interactions between active sites in PPy and fMWCNTs. After addition fMWCNT, we note a slight change in bonds position and a decrease in the intensity as shown in Table (2)

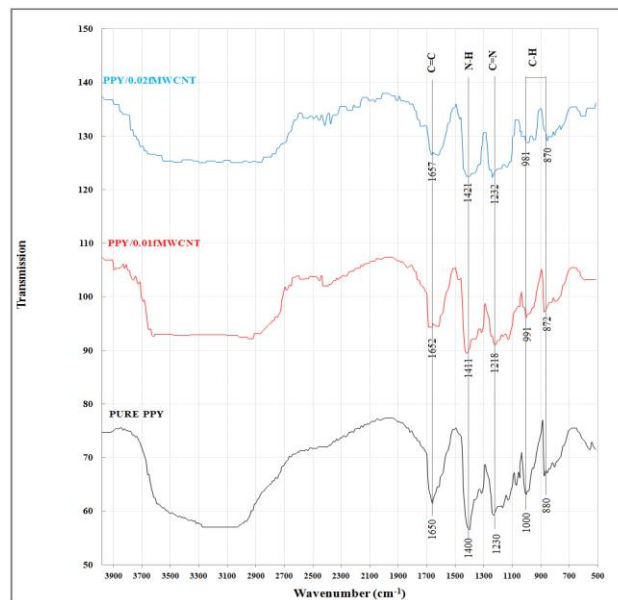


Fig.(6). FTIR spectra of the PPy and (PPy/fMWCNT) thin films

Table 2 shows the value of bonds for (PPy/fMWCNT) films through a FTIR analysis

Sample	C=C	N-H	C=N	C-H
PURE PPy	1650	1400	1230	1000 880
PPy/0.01CNT	1652	1411	1218	991 872
PPy/0.02CNT	1657	1421	1232	981 870

4. Conclusions

In the concluding conclusions, we have synthesized PPy and (PPy/fMWCNT) nanocomposite by electrochemical polymerization method. From X-ray studies revealed that thin films are polycrystalline. The FE-SEM of surface morphology and also studied. The optical band gap of the thin films changed from 2.4 to 2.09 eV as concentration of CNT increased from 0.01 to 0.02 M, which indicates that it is dependent on the film stoichiometry. Proper formation of all thin films in a conducting form was established by FTIR. The SEM of surface morphology and also studied.

Reference

1. A. Ion, A. Popescu, M. Ungureanu, J. C. Moutet, and E. Saintaman. (1997). A ferrocene crown ether-functionalized polypyrrole film electrode for the electrochemical recognition of barium and calcium cations. *Adv. Mater.* 9(9) 711-713.
2. A. Heller. (1990). Electrical wiring of redox and enzymes. *Acc Chem Res*, 23,128-134.
3. N. Gupta, S. Sharma, I. A. Mir, and D. Kumar. (2006). Advances in sensors based on conducting polymers. *Journal of Scientific &Industrial Research Journal of Scientific and Industrial Research*, 65, 549-557.
4. J. h. Chen, Z. P. Huang, D. Z. Wang, S. X. Yang, W. Z. Li, J. G. Wen, and Z. F. Ren. (2002). Electrochemical synthesis of polypyrrole films over each of well-aligned carbon nanotybes. *Synthetic metals* 125, 289-294.
5. A. K. Bakhshi. (1995). Electrically conducting polymers: from fundamental to applied research. *Bull. Mater. Sci.* 18(5), 469.
6. S. H. Kim, S. H. Jang, S. W. Byun, J. Y. Lee, J. S. Joo, S. H. Jeong, and M. J. Park. (2003). Electrical properties and EMI shielding characteristics of polypyrrole-nylon 6 composite fabrics. *J. Appl. Polym. Sci.* 87, 1969-1974.
7. S. Iijima, (1991). Helical microtubules of graphitic carbon. *Nature* 354 (7), 56-58.
8. C. A. Grimes, C. Mungle, D. Kouzoudis, S. Fang, and P. C. Eklund. (2000). The 500 MHz to 5.50 GHz complex permittivity spectra of single-wall

- carbon nanotube-loaded polymer composites. *Chem. Phys. Lett.*, 319,460-464.
9. S. Shiraishi, and A. Oya. (2003). Electric Double Layer Capacitance Properties of Carbon Nanotubes and Carbon Nanofibers - The Present State as Capacitor Electrode. *Electrochem.* 71, 887.
10. Ch. Ernegger, Ph. Mauron, P. Sudan, P. Wenger, V. Hermann, R. Gallay, and A. Zuttel. (2003). *J. Power Sources* 124, 321.
11. G. A. Snook, G. Z. Chen, D. J. Fray. M. Hughes, and M. Shaffer. (2004). Studies of deposition of and charge storage in polypyrrole-chloride and polypyrrole-carbon nanotube composites with an electrochemical quartz crystal microbalance. *Journal of Electroanalytical Chemistry*, 568, 135-142.
12. M. Hughes, G. Z. Chen, M. S. P. Shaffer, D. J. Fray, and A. H. Windle . (2004). Controlling the nanostructure of electrochemically grown nanoporous composites of carbon nanotubes and Conducting polymers. *Composites Science and Technology* 64, 2325-2331.
13. S. Paul, Y. S. Lee, J. A. Choi, Y. C. Kang, and D. W. Kim. (2005). Synthesis and Electrochemical Characterization of Polypyrrole / Multi-walled Carbon Nanotube Composite Electrodes for Supercapacitor Applications. *Bull. Korean Chem. Soc.*, 31(5), 1228-1232.
14. B. Zhang, Y. Xu, Y. Zheng, L. Dai, M. Zhang, J. Yang, Y. Chen, X. Chen, and J. Zhou. (2011). A Facile Synthesis of Polypyrrole / Carbon Nanotube Composites with Ultrathin, Uniform and Thickness-Tunable Polypyrrole Shells. *Nanoscale Research Letters*, 6, 431.
15. Huang, J. E., Li, X. H., Xu, J. C., and Li H. L. (2003), Well-dispersed single-walled carbon nanotube/polyaniline composite films. *Carbon*, 41, 14, 2003, 2731-2736.
16. Xu, Q., Meng, G., Han, F., Zhao, X., Kong, M., and Zhu, X. (2009). A novel one-step method to synthesize copper nitrate hydroxide nanorings. *Mater. Lett.*, 19, 2, September 2009, s480-s484.
17. Sivakkumar, S. R., Mac Farlane, D. R., Forsyth, M., and Kim, D. W. J. (2007). Ionic Liquid-Based Rechargeable Lithium Metal-Polymer Cells Assembled with Polyaniline/Carbon Nanotube Composite Cathode. *Electrochem. Soc.*, 154. A834.
18. Attout, A., Yunus, S., Bertrand, P. (2008). Electroless deposition of polyaniline: synthesis and characterization. *Surf. Interface Anal.*, 40, 657-660.
19. P. Hojati Talemi, and G.P.Simon. (2010). Electropolymerization of Polypyrrole / Carbon Nanotube Nanocomposite Films over an Electrically Nonconductive Membrane. *J. Phys. Chem. C*, 114, 13962-13966.
20. Hughes, M. S. P. Shaffer, A. C. Renouf, C. Singh, G. Z. Chen, D. J. Fray, and A. H. Windle, (2002). Electrochemical capacitance of nanocomposite films formed by coating aligned arrays of carbon nanotubes with polypyrrole. *Advanced Materials*, 14, 5, 382-385.
21. B. Lakard, S. Carquigny, O. Segut, T. Patois, and S. Lakard. (2015). Gas

- Sensors Based on Electrodeposited Polymers Metals, 5, 1371-1386.
22. S. G. Bachhav, D. R. Patil. (2015). Study of Polypyrrole-Coated MWCNT Nanocomposites for Ammonia Sensing at Room Temperature. Journal of Materials Science and Chemical Engineering, 3, 30-44.
23. G. A. Kadhim and M. H. Suhai. (2019). The Nanocomposite Film of Polypyrrole and Functionalized Single Walled Carbon Nanotubes as Gas Sensor of NO₂ Oxidizing Gas. Indian Journal of Natural Sciences, 9 (52), 16536-16543.
24. D. N. Aswal, S. K. Gupta, Nova Sincience publishers. Inc, 51 (2007) 33-93.
25. D. N. Huyen, N. T. Tung, T. D. Vinh, and T. D. Thie. (2012). Synergistic Effects in the Gas Sensitivity of Polypyrrole/Single Wall Carbon Nanotube Composites. Sensors. 12, 7965-7974.