The DC electrical conductivity of prepared pure polypyrrole and polypyrrole /graphene (PPY/GN) nanocomposite by in-situ polymerization

Fatima Mikdad Ahmed, Salma Mohammad Hassan, Mohanad Irzooqi Kamil

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

E-mail: physistfatma@gmail.com

Abstract

In this work, pure Polypyrrole (PPy) and Polypyrrole (PPy)/ Graphene (GN) was synthesized by in-situ polymerization with different weight percentages (0.1, 0.3, 0.5, 1, 3 and 5 wt.%) of GN nano particles using chemical oxidation method at room temperature. The FTIR, SEM and electrical properties were studies for the nano composites. The result show that when concentration of GN Nano particle increase, the electrical conductivity increased and the graphene sheets were merging to form a continuous area of the GN through the polypyrrole base material. The FTIR spectra shows that the characteristics absorption peaks of polypyrrole that is,1546.80, 1463.87 and 3400.27 cm^{-1} (stretching vibration in the pyrrole ring), and at 1080.06 cm^{-1} was assigned to C—O stretching and at 1589.23 cm^{-1} was assigned to C—C vibration of carbon ring in graphene.

التوصيل الكهربائي المستمر للمتراكب النانوي لبولي يايرل النقي و بايرل/ كرافين المحضر بطريقة البلمرة

فاطمة مقداد احمد، سلمى محمد حسن، مهند ارزوقي كامل

قسم الفيزياء، كلية العلوم، جامعة بغداد

الخلاصة

في هذا العمل تم تحضير البولي بايرول النقي و البولي بايرول/ الكرافين بدرجة حرارة الغرفه بطريقة الاكسدة الكيميائية و قد تم استخدام جسيمات الكرافين النانوية و بالنسب التالية (% 5 , 3 , 1 ,0.5 ,0.3 ,0.1). و تم استخدام طيف الاشعه تحت الحمراء و المجهر الالكتروني و كذالك الخصائص الكهربائية تم دراستها للمتراكبات النانوية. اظهرت النتائج ان بزيادة جسيمات الكرافين النانوية تزداد التوصيلية الكهربائية و صفائح الكرافين تندمج مكونه منطقه مستمرة من الكرافين مع المادة الاساس للبولي بايرول. طيف الاشعة تحت الحمراء اظهر قمم امتصاص مميزة للبولي بايرول و هي عند ال 1546.80 و 1463.87 و 3400.27 (مط اهتزازي في حلقة البايرول) و 1080.06 تمثل اصرة مط C—O و 1589.23 تمثل اصرة اهتزاز C—C حلقة الكاربون في الكرافين.

Introduction

The development of conductive polymers has given a new dimension to the present time. Conducting polymers are a possible class of new materials that combine solubility, processability and flexibility of plastics with electrical and optical properties of metals and semiconductors [1]. Polymers are known so far as a class of heat-sensitive, flexible, electrically insulating and amorphous materials. Electrically conducting polymers appear to be ideal applicants for

different applications, as many of their properties surround problems common with traditional materials, including corrosion, weight, matrix incompatibility, and environmental integrity [2]. In addition to being corrosion resistant and lightweight, many critical properties of conducting polymers may be designed for different applications. The strength to weight, possibility, resistance to corrosion, has

given conducting polymers advantage over metals [3] Conducting polymers are made up of carbon and hydrogen, along with hetero atoms such as nitrogen or Sulphur [4]. All conducting polymers have π-conjugation across the polymer backbone; typical conducting polymers include polyaniline (PANI), polypyrrole (PPy), polythiophene and polyacetylene. These are shown in Fig.1 [5].
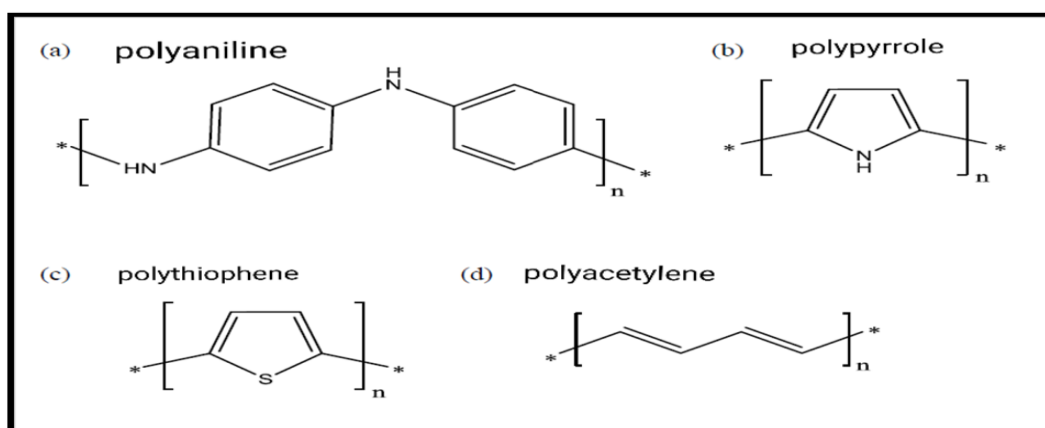

Fig.1: The structures of conducting polymers shown uncharged (a) polyaniline, (b) polypyrrole, (c) polythiophene and (d) polyacetylene [5].

Conjugated conducting polypyrrole (PPY) has been well known for many years which can be synthesized either chemically or electrochemically [6]. Polypyrrole is one of the promising conducting polymers applied in the industry and new technology with unique properties, such as relatively high conductivity, easy synthesis, and high mechanical and chemical stability [7]. Among the conjugated polymers, polypyrrole (PPy) is the

most attractive one for its simple polymerization and wide application in gas sensors, electrochromic devices, and batteries [8]. Polypyrrole can be produced in the form of powders, coatings, or films. It is intrinsically conductive, stable and can be quite easily produced also continuously [9]. Polypyrrole, is chemical compound formed from a number of connected pyrrole ring structures as shown in Fig.2 [10].
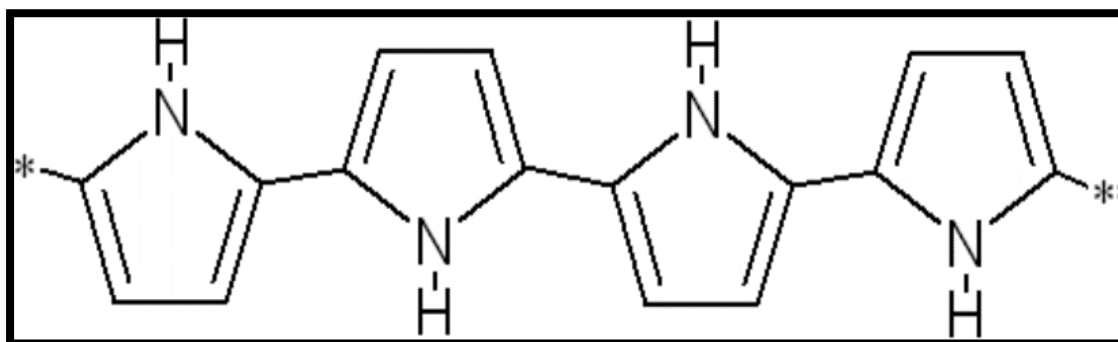

Fig.2: The structure of polypyrrole (PPY) in the neutral state [10].

Materials and methodology

Pyrrole monomer (mPPy) with purity 98% was supplied by Sigma Aldrich, ferric chloride (FeCl$_3$) with purity 98%, was supplied by Himedia Laboratories Pvt. Ltd, which was used as the oxidizing agent, Graphene (GN) with purity 98%was supplied by USA-with (6-8) nm. And Dimethely sulfoxide (DMSO) with purity 99.6% was supplied by BDH-England.

In this work easy purification was used, which is based on differences in the boiling point of the liquids. The mixture is heated to (110 -180) ℃ to change the most volatile component from the liquid into steam. The pyrrole steam passes into a condenser, and the steam was cooled to get a clear liquid of pyrrole as shown in Fig.3.
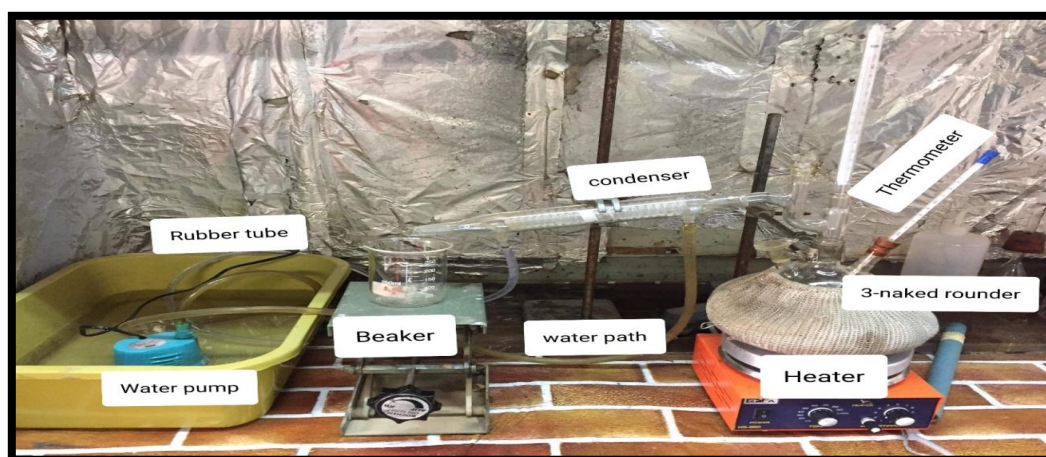

Fig.3: The procedure steps of the purification of Pyrrole (Py).

Polypyrrole (PPy) and PPy/GN were synthesized by chemical oxidative in-situ polymerization technique using pyrrole monomer and ferric chloride (FeCl$_3$) as oxidant. Pure polypyrrole was prepared by adding of (2 mL) of pyrrole to (150 ml) of distilled water in a beaker and stirred for (10 min.), (3 g) of ferric chloride was added to solution of pyrrole slowly and stirred for (4-5 h.) at room temperature (23 ℃), the polypyrrole precipitate was collected by filtration, washed with distilled water for several times and dried in an oven at 70 ℃. In a similar way, PPy/GN was prepared by adding graphene nanoparticle powder with different weights percentage (0.1, 0.3, 0.5, 1, 3, and 5 wt.%).

The morphological examination of PPy and PPy-GN nanocomposite was carried out using scanning electron microscope (FEL, INSPECT S50). The chemical structure was characterized by FTIR spectroscopy (Shimadzu FT-IR 8000 series) in the range of 400–4000 cm^{-1}.

D.C electrical measurements were used to investigate pure PPy and PPy/GN nanocomposites. The polypyrrole powder was thoroughly grounded in a mortar to obtain very fine particles, and then it was compressed under a pressure of (8 tones) to gate samples as a pellet. The resulting pellet has a diameter of (1.3 cm and a thickness of 0.112 - 0.137 cm). A series circuit was used for the D.C electrical measurements as shown in Fig.4. The sample was placed in a holder specially designed to minimize lost capacitance (guard ring electrode methods) as shown in Fig.5. With range of temperature was (303-453) k.
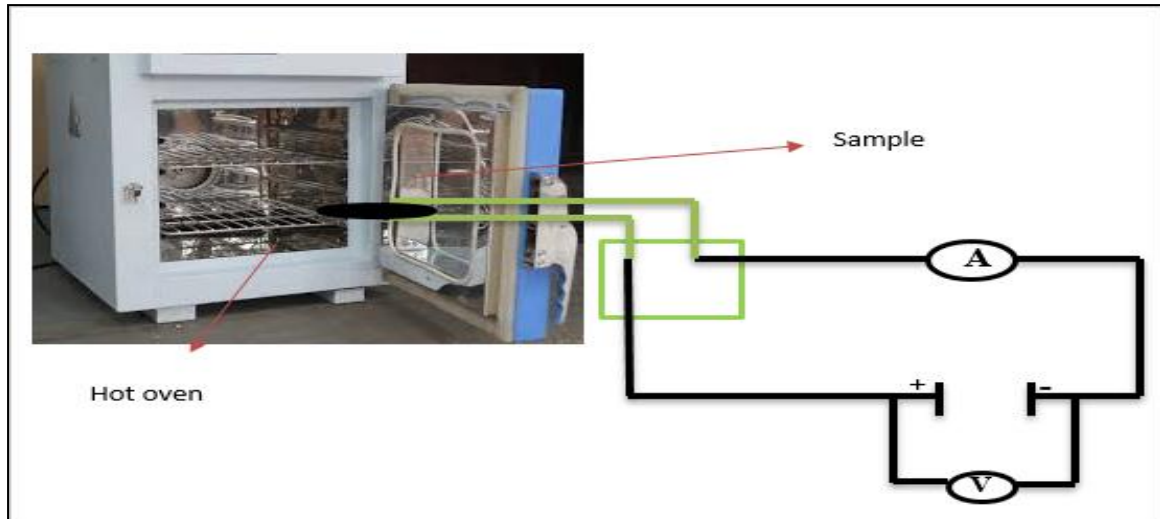
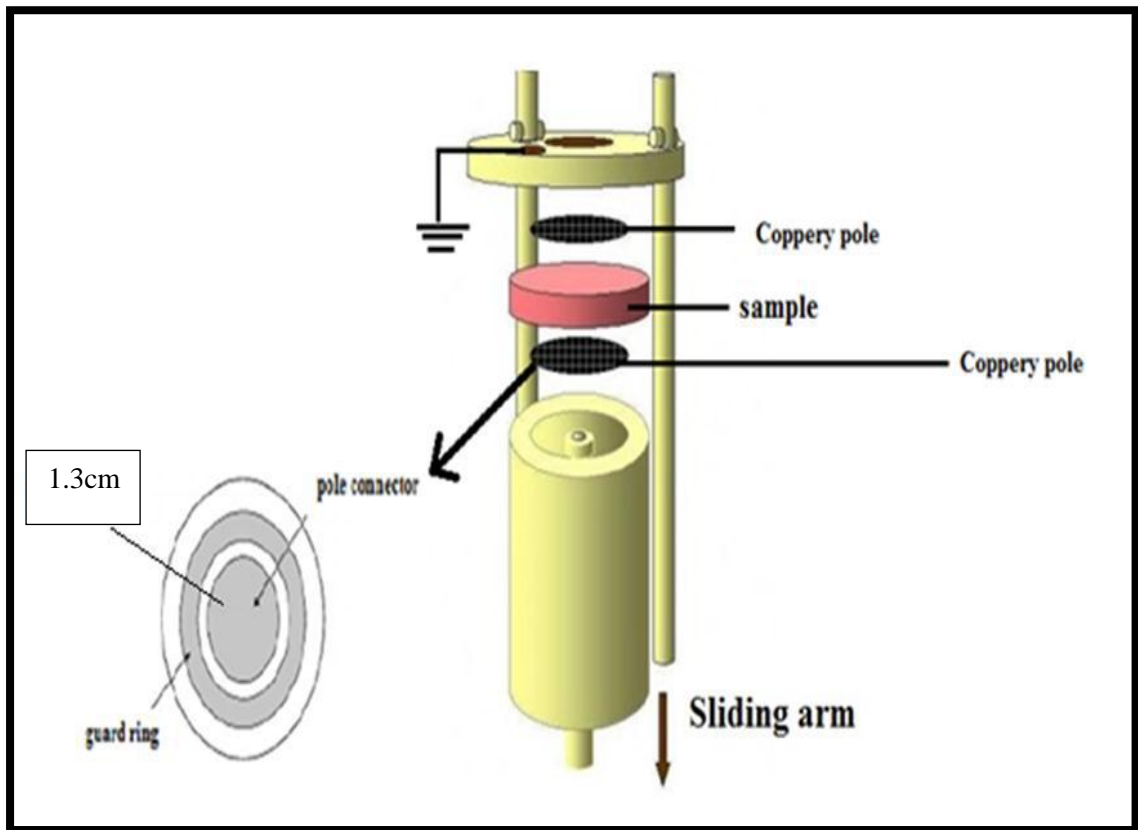**Fig.4: Schematic diagram of the series circuit of DC measurement.**

Fig.5: Schematic diagram of used electrode.

The total conductivity was calculated by using the following equation [11]:

$$\sigma = \frac{d}{RA} \qquad (1)$$

where R is the resistance, which is the ratio between desired applied test voltage and the current passing through the test sample which is measured by the electrometer, d is the average thickness of the sample, and A is the guard electrode effective area. In this model, the electrodes Fig.4 have a circular area with

$$A = \frac{D^2\pi}{4} \qquad (2)$$

where D=1.3 cm^2

Arrhenius equation was used to obtain the Activation Energy (E_a) in J by the following formula [11]:

$$\sigma = A \, exp\left(-\frac{\dot{E}_a}{k_B T}\right) \qquad (3)$$

K_B is the Boltzmann's constant which is 1.3806×10^{-23} J/K, T is the temperature in Kelvin. The E_a is in practice taken to be the slope of an Arrhenius plot of ln (σ) versus $1/T$ in Kelvin [12].

Result and discussion

In Fig.6, the bands appear at 1546.80, 1463.87 and 3400.27 cm^{-1}, for pure PPy, were assigned to the C–C, C=C, and N–H stretching vibration in the pyrrole ring. While the bands at 2848.67 and 2918.10 cm^{-1} were assigned with the symmetric and asymmetric vibrations of CH$_2$.
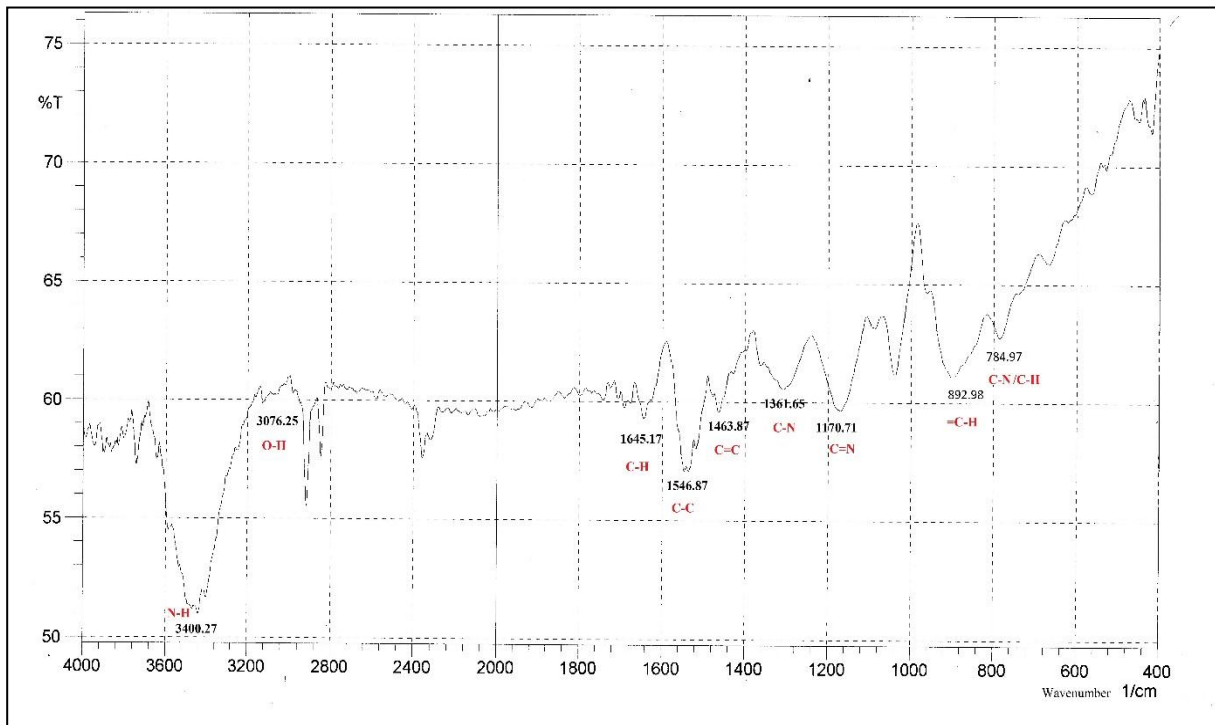

Fig.6: FTIR spectra of pure PPy.

The characteristic bands of GN was shown in Fig.7 at 1080.06 cm^{-1} was assigned to C—O stretching and at 1589.23 cm^{-1} was assigned to C—C vibration of carbon ring in graphene, the band observed in 2823.19 cm^{-1} attributed to C=O stretching [13].
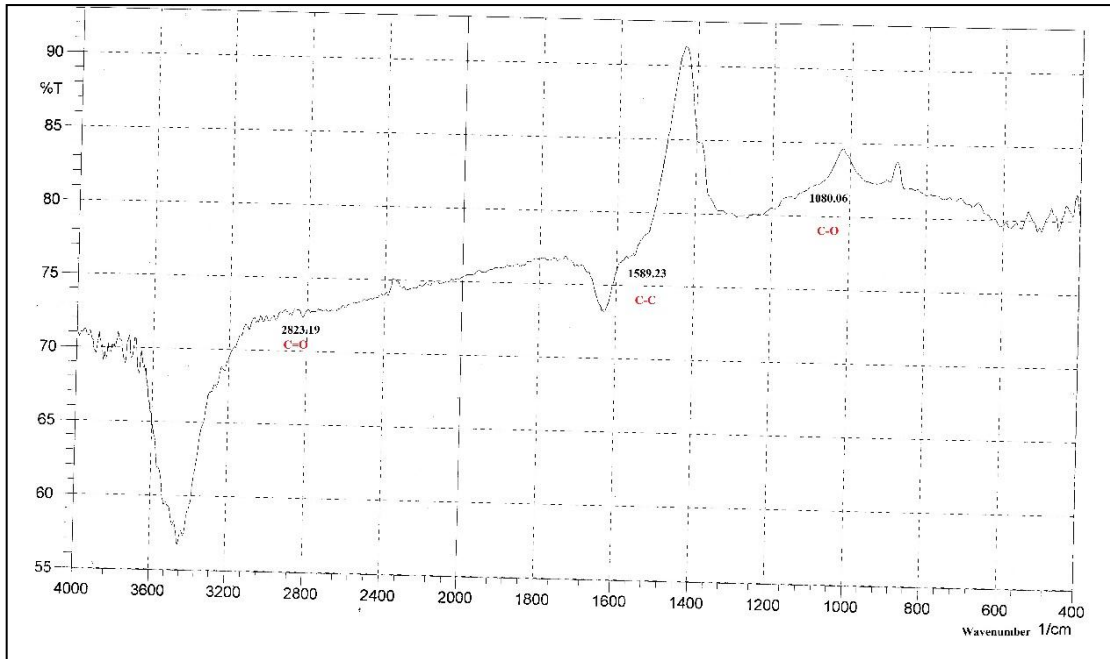
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Fig.7: FTIR spectra of pure GN.

The characteristic bands of PPy and GN are also observed for the nanocomposites but, it has a shift in the peaks because of the interaction between the PPy and GN surface, Fig.8. It can be seen that there is a distinct absorption band from 779.19-786.9 cm^{-1} was attributed to C—N stretching and C—H bending mode of benzenoid ring. A band at (856.34-966.27) cm^{-1} may be assigned to =C–H bending. A band at (1039.56-1045.06) cm^{-1} was attributed to C–O stretching. Band at (1170.71-1180.35) cm^{-1} attributed to C=N stretching. Bands at (1294.15-1392.51) cm^{-1} were assigned to C—N stretching (aromatic amine). Bands observed in (1433.01-1487.01) cm^{-1} was assigned to C=C of ring stretching mode and at (1515.94-1558.38) cm^{-1} was assigned to C-C vibration of Py rings. Bands at (2833.24-2975.96) cm^{-1} were attributed to C=O stretching of graphene. Band at (3066.61-3107.11) cm^{-1} was attributed to O-H stretching. Bands at (3371.34-3541.06) cm^{-1} were assigned to N-H stretching the obtained result agrees with [14-16].
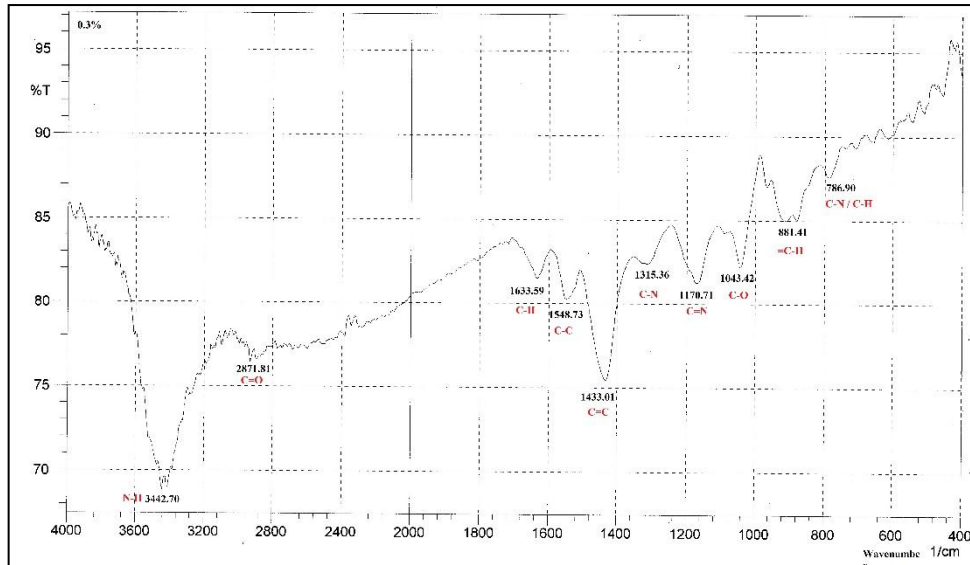
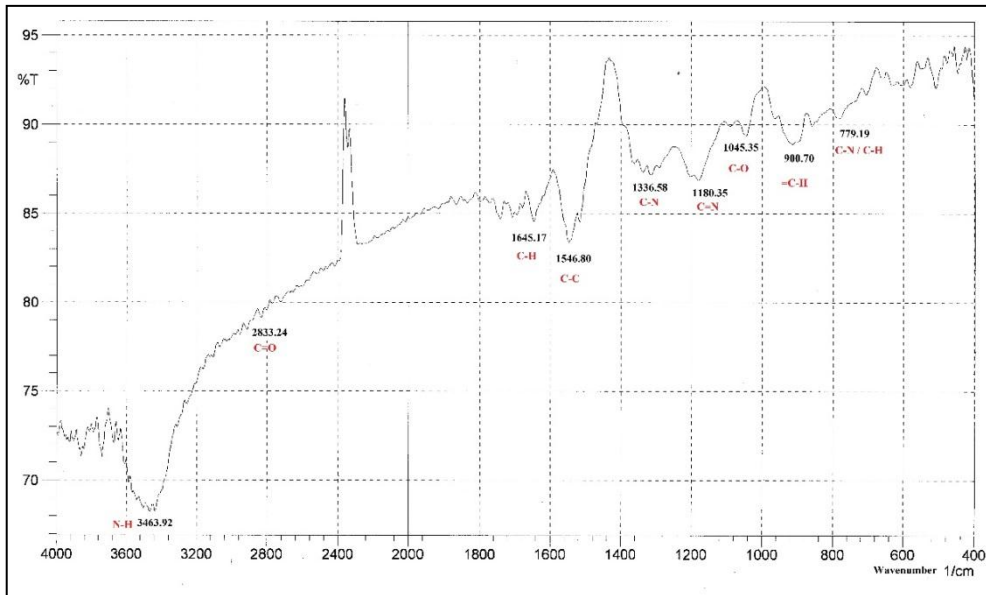*Fig. 8: (a) FTIR spectra of PPy with (0.3%) of GN nanocomposite.*

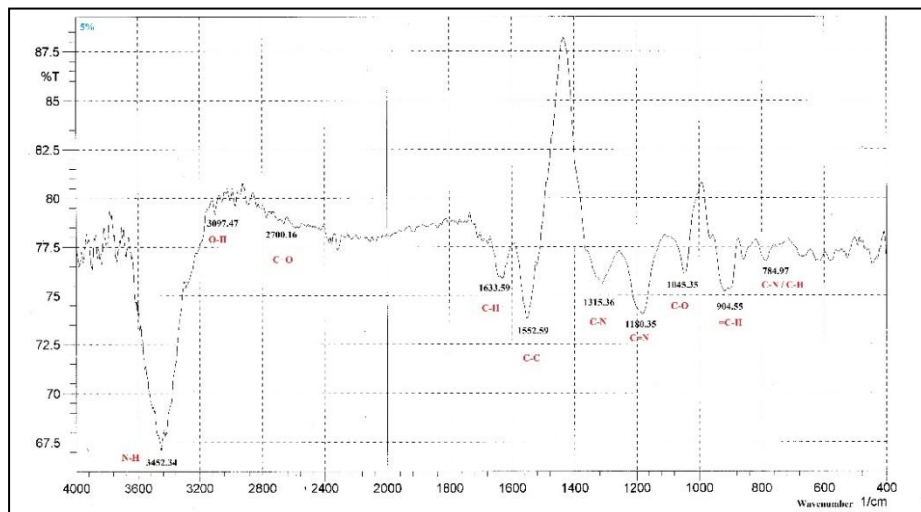*Fig.8: (b) FTIR spectra of PPy with (3%) of GN nanocomposite.*

Fig.8: (c) FTIR spectra of PPy with (5%) of GN nanocomposite.

The PPy was solid, agglomerated spheres, with size ranging from 9.887 nm to 150.7 nm as shown in Fig.9(a).

From Fig.9(b) it can be seen GN sheet(laminate) is compact with granular morphology of PPy. When increased the concentration of CN nanoparticle to 5% as shown in Fig.9(c), the merging of the graphene sheets to form a continuous area of the GN through the polypyrrole base material was observed [17].
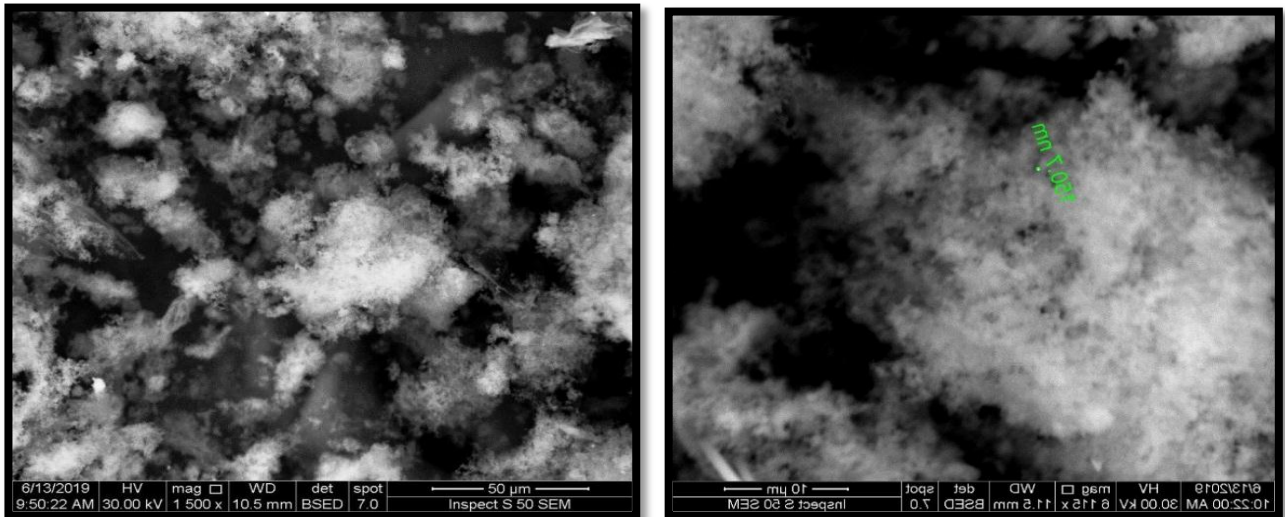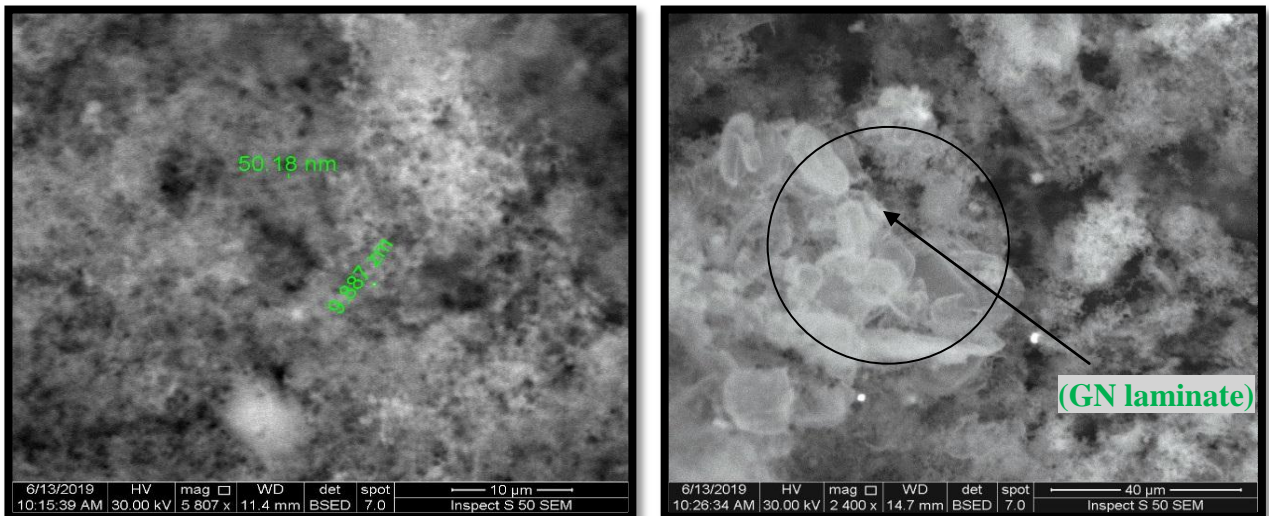

Fig.9: (a) SEM for pure PPy.

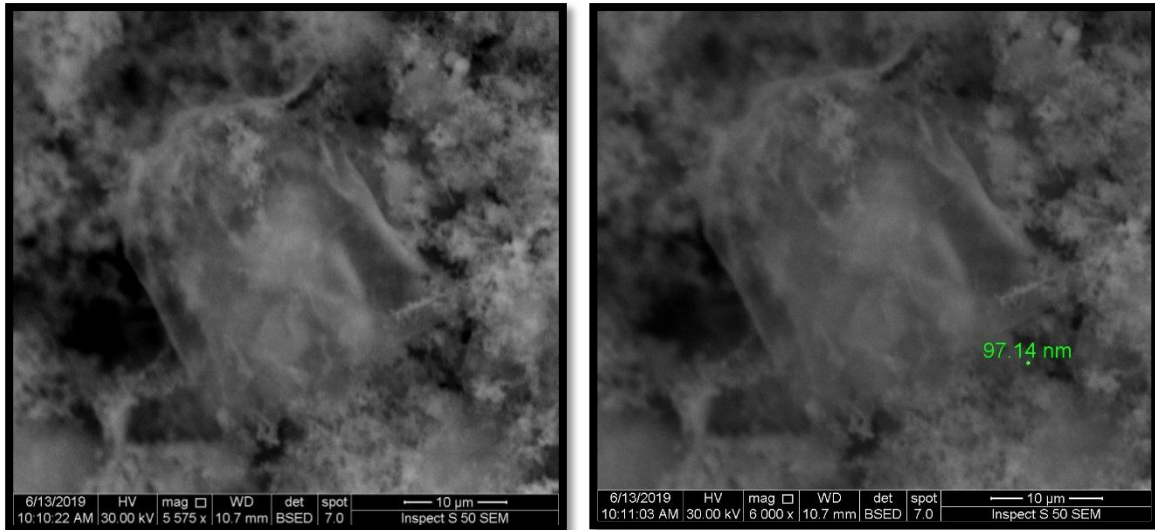

Fig.9: (b) SEM for PPy with 3%GN.

Fig.9: (c) SEM for PPy with 5%GN.

The conductivity of polypyrrole is interchain charge transport. The charge transport mechanism depends on the temperature and doping level. The DC conductivity varies with the GN concertation and the temperature. It is increasing with both GN concentration and temperature about four order of magnitude as listed in Table 1. Fig.10 shows the DC conductivity varies exponentially according to Arrhenius Eq. (3).

Table 1: The electrical conductivity as a function of temperature.

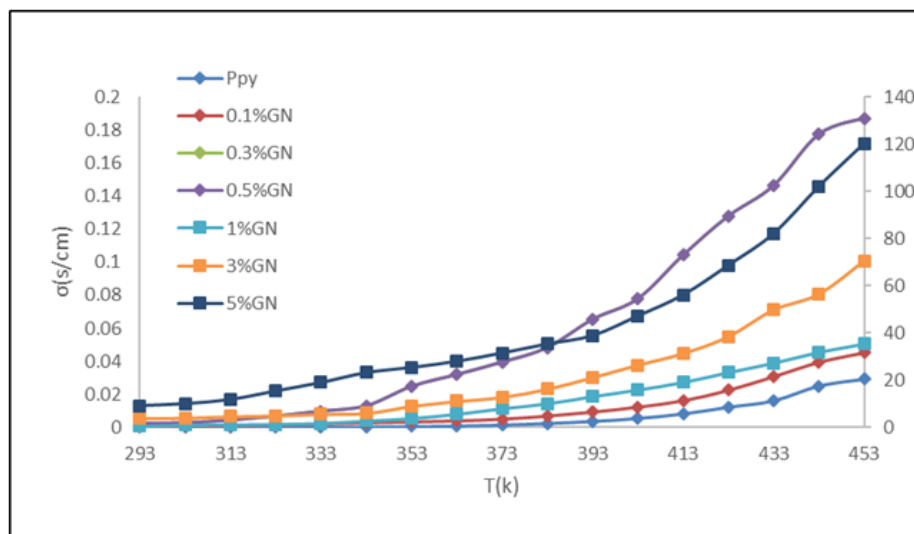| samples	Min. Conductivity (S./cm)	Max. Conductivity (S./cm)
PPy	1.9×10^{-5}	0.029
0.1%GN	7.5×10^{-4}	0.045
0.3%GN	2.5×10^{-3}	0.187
0.5%GN	2.7×10^{-2}	3.14
1%GN	0.48	35.31
3%GN	3.85	70.35
5%GN	10.09	120.28

Fig.10: The D.C electrical conductivity with temperature for PPy/GN nanocomposite.

Fig.11 shows the variation of conductivity for doped polypyrrole within the range of (303 – 453) k as a function of reciprocal temperature. It can be seen from this Figure that all sample have nearly single activation energy. It can be found that the conductivity increases with increasing the concentration percentage of GN (0.1, 0.3, 0.5, 1, 3 and 5) wt.% (g), the activation energy for pure PPy is higher than that of PPy/GN nanocomposites as listed in Table 2 [18, 19].
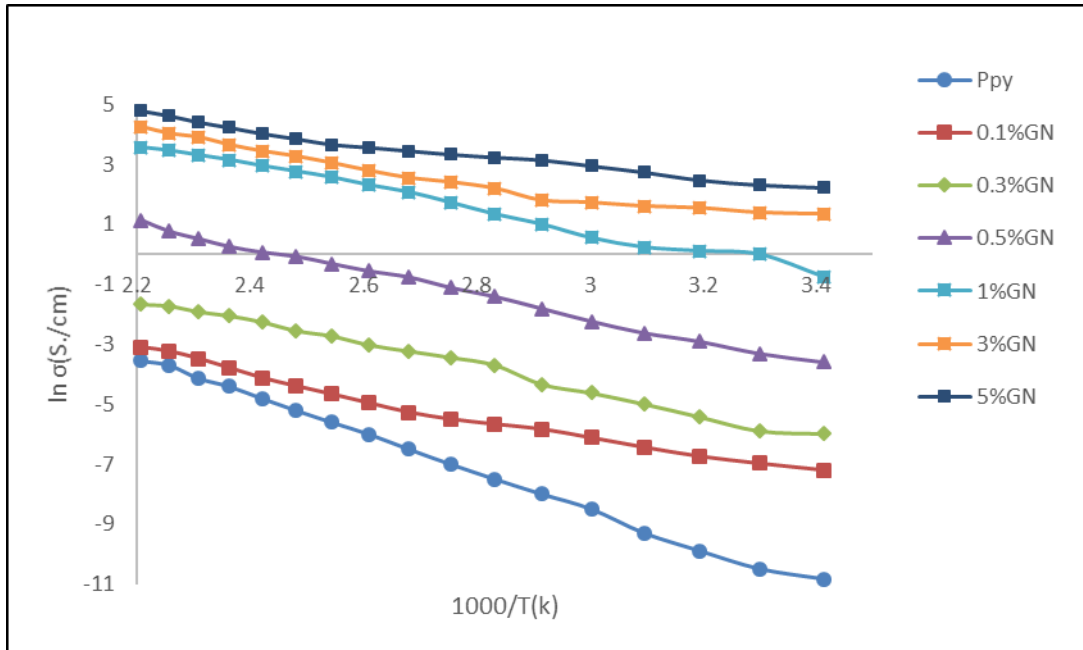

Fig.11: The variation of DC electrical conductivity as a function of reciprocal temperature.

Table 2: Activation energy data for all investigated samples.

Samples	Slope	Activation Energy (eV)
PPy	10.883	0.935938
0.1%GN	7.869	0.666734
0.3%GN	7.541	0.648526
0.5%GN	7.462	0.6417578
1%GN	5.0966	0.43830
3%GN	4.9452	0.4252872
5%GN	2.169	0.186534

The variation of electrical conductivity as a function of the filler content at temperature 303 k and 453 k was shown in Fig.12. When GN concentration increased the conductivity increased because the GN particle make connected path through the PPy matrix according to the percolation theory, where the nanofiller inside the polymer matrix can come close to each other and form an effective conductive path which reduces resistance in the nanocomposites structure that mean the conductivity of GN which dominated as shown in Fig.13, our result agree with [17]
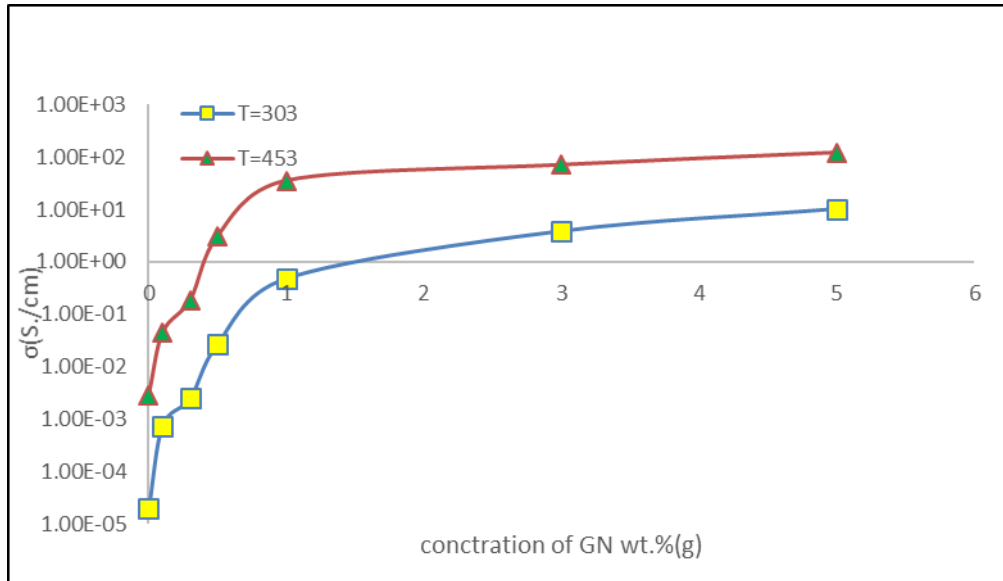
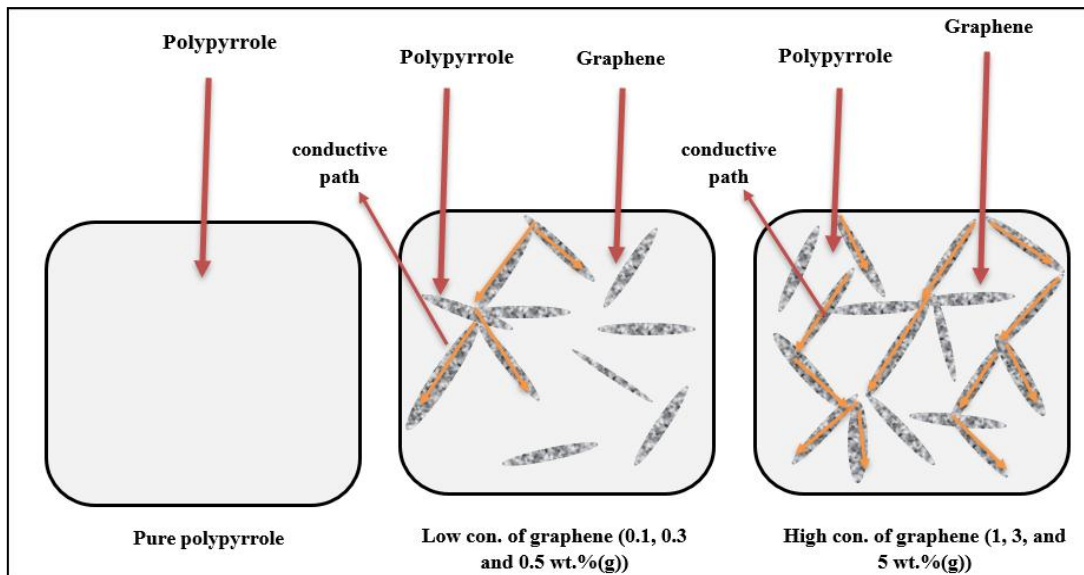*Fig.12: The variation D.C electrical conductivity with GN wt.% concentration.*

Fig.13: Configuration of GN in PPy matrix.

Conclusions

In this work, simple distillation method was used to get pure polypyrrole. The PPy and PPy/GN nanocomposites were prepared from the oxidation 2 ml pyrrole with 3 g of ferric chloride in aqueous medium. FTIR confirms the prepared of PPy, SEM images showed that the nanocomposites had sheet like morphology. SEM images revealed that GN was well distributed on the PPy surface. Measurements of DC electrical conductivity shows that the conductivity increase about four orders of magnitude with both increases in temperature and GN concentration.

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