Optical and A.C. Electrical Properties for Polypyrrole and Polypyrrole/Graphene (ppy/gn) Nanocomposites

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Abstract
In this work, chemical oxidation was used to polymerize conjugated polymer "Polypyrrole" at room temperature Graphene nanoparticles were added by in situ-polymerization to get (PPY-GN) nano. Optical and Electrical properties were studied for the nanocomposites. optical properties of the nanocomposites were studied by UV-Vis spectroscopy at wavelength range (200-800 nm). The result showed optical absorption spectra were normally determined and the result showed that the maximum absorbance wave length at 280nm and 590nm. The optical energy gap has been evaluated by direct transition and the value has decreased from (2.1 eV for pure PPy) to (1.3 eV for 5 %wt. of GN). The optical constants such as the band tail width ΔE was evaluated, the value of ΔE for pure PPy was (0.0949eV) while for 5 wt. % of GN it was (0.5156 eV), It has been observed that the Urbach tail for pure PPy was smaller than that for PPy/GN nanocomposites and it increase as GN concentration increases. The A.C electrical conductivity at range of frequency (10^3 Hz-10^6 Hz) was increased by increasing the frequency and GN concentration about four order of magnitude. The s value was about (0.653-0.962) which means that the mechanism of conductivity is correlated hopping mechanism (C. H. P.). The dielectric constant and dielectric lose were determined and found to decrease with increasing frequency.

1. Introduction
Polypyrrole (PPy) is a chemical material consisted of a number of joined pyrrole rings [1]. Polypyrrole (PPy) is a nondegenerate ground state polymer with two types of chain arrangement including repeating units of aromatic as well as quinoid [2], as shown in Figure (1). Pure polypyrrole (PPy) with benzenoid structure is an insulator in nature, so it needs to be oxidant by doping to act as a semiconductor [3].

Figure 1: The Structures of polypyrrole (Aromatic and Quinoid) [3].

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Polypyrrole (PPy) is most attractive for its simple polymerization and many application in optical switching divides, anti-static films, light emitting diodes, electromagnetic shielding layer, electro-chromic devices, electrode for batteries, photovoltaic, and gas sensors[4, 5], moreover Polypyrrole (PPY) is used in the design of solid-state electronic devices such as metal-insulator-semiconductor FET structures and metal-semiconductor because of the availability of a wide range of energy band gaps[6].

A feature of a conductive polymer is the presence of conjugated double bands across the polymer backbone. In conjugation, the bands between the carbon atoms are alternate. Single double and single. Every band has a localized sigma (σ) band which composes a strong chemical band, and every double band have delocalized pi (π) band which is a lower strength chemical band. However, conjugation is not enough, to make the polymer material conductive. Furthermore, to the presence of the double bonds, doping adds charge carriers in the shape of extra electrons or holes into the polymer matrix which results in increasing its electrical conductivity [7, 8].

2. Experimental work

Pyrole monomer(mPy) with purity 98% was supplied by Sigma Aldrich company. Ferric chloride (FeCl₃) with purity 98%, was supplied by Himedia Laboratories Pvt. Ltd, which was used as the oxidizing agent. Graphene (GN) with purity 98% and with a diameter of (6-8) nm was supplied by USA-diameter (6-8) nm Dimethely sulfoxide (DMSO) with purity 99.6% was supplied by BDH-England.

2.1. Synthesis of pure Polypyrrole (PPy) and PPy/GN

Polypyrrole (PPy) and PPy/GN were produced by chemical oxidative in-situ polymerization technique the use of pyrrole monomer and ferric chloride (FeCl₃) as oxidant. Pure polypyrrole was prepared by adding (2mL) of pyrrole to (150 ml) of distilled water in a beaker and stirred for (10 minutes). (3 g) of ferric chloride was added slowly to the pyrrole solution and stirred for (4 - 5 hours) at room temperature (23 ⁰C). The polypyrrole precipitate was obtained by filtration, washed several times with distilled water and dried in an oven at 70 ⁰C for six hours. In the same way, the PPy/GN nanocomposites were prepared, but different weights (0.1, 0.3, 0.5, 1, 3 and 5 wt. %) of graphene nanoparticles were added during polymerization.

2.2. Sample Preparation for UV-Vis. Measurements

Polypyrrole and PPy/GN nano-composites of 0.05 g weight were dissolved in 5 ml DMSO. The solution was stirred with a magnetic stirrer for more than two hours to achieve a homogenous solution. A Shimadzu UV-Vis. spectrophotometer in the wavelength range 200 – 800 nm was used to is a term that is used to describe the absorption of a substance. The absorption spectra of the prepared samples. The optical energy gap was estimated using the absorption spectrum.

2.3. Sample Preparation for Electrical properties

AC electrical measurements were employed to investigate pure PPy and PPy/GN nanocomposites. The polypyrrole was thoroughly grounded in a mortar to obtain very fine particles, and then it was compressed under a pressure of (8 tones) to get the samples as pellets. The resulting pellet has a diameter of (1.3 cm) and a thickness of (0.112 - 0.137cm), as shown in Figure (2). The sample was placed in a holder specially designed to minimize lost capacitance and leakage current (guard ring electrode methods), as shown in Figure (3).
3. Results and discussion

3.1. Optical Properties

The optical properties of PPy and PPy/GN were recorded by UV-visible spectra, in the wavelength range of (200-800) nm. The absorption versus wave length and optical energy gap have been evaluated.

3.1.1. Absorption of UV-Vis. spectroscopy

The optical absorption spectrum, obtained by UV-spectroscopy, of PPy and PPy/GN are shown in Figure 4(a-b). The absorption spectra have two peaks (maximum absorbance). One, that can be seen at wavelength 300nm, belongs to $\pi \rightarrow \pi^*$ and the other at 580 nm is due to $n \rightarrow \pi^*$. It was observed that the maximum absorption at the UV region was shifted towards lower wavelengths with increasing the GN concentration, it was at 280 nm and 590 nm, respectively.

3.1.2. Optical Energy Gap

Tauc put the empirical equation of optical energy gap and energy of incident photon which is [9]

$$\alpha h \nu = A \left( h \nu - E_g \right)^n \ldots \ldots \ldots (1)$$
where A is a constant, hν energy of incident photon, which can be calculated using the equation $h\nu = 1240/\lambda \text{ (nm)}$. And, depending on the type of the electronic transition, $r$ is the optical transition order. If the extremities of V.B. and C.B. are at the same location in k – space, the transition is termed direct, but if the transition is only achievable with phonon aided ($k\neq 0$), it is called indirect. As a result, the allowed direct, allowed indirect, banned direct, and forbidden indirect transitions have values of $1/2$, $2$, $3/2$, and $3$, respectively [10].

The plots of $(ah\nu)^2$ versus photon energy $h\nu$ were used to evaluate the optical energy gaps. A typical plot for pure PPy and PPy/GN are shown in Figure (5-a), (5-b), respectively. It can be seen, all samples exhibit a direct optical energy gap, as seen in this diagram. The energy reduced as the concentration % of GN increased from (2.1–1.3) eV, indicating that the reduction in the optical band gap is probably due to the modification of the polymer structure.

### 3.2. A.C. Conductivity

The A.C. conductivity for conducting polymer changes with frequency according to the following formula [11]:

$$\sigma_{AC}(\omega) = A \omega^r \quad \ldots \ldots (2)$$
where: $A$ is a constant parameter $\omega = \text{angular frequency} = 2\pi f$ (f is the linear frequency), and $(s)$ is the frequency exponent. The conductivity ($\sigma$), dissipation factor (D) and the resistance (R) were measured with a computerized sensitive impedance analyzer in the frequency range (10 KHz – 10 MHz) at room temperature. Figure (6) shows the frequency dependence of the measured A.C. conductivity for pure PPy and PPy/GN nanocomposites.

The value of A.C conductivity changed from $(6.16 \times 10^{-6} – 8.1 \times 10^{-2})$ (S/cm) for pure PPy. The conductivity increased by four orders of magnitude with frequency in the same time the A.C conductivity changed with increasing concentration of GN particles from $(1.6 \times 10^{-5} – 2.6 \times 10^{-2})$ (S/cm) when the concentration changed from $(0.1\% \rightarrow 5\%)$ at 10kHz, as shown in Figure (7).

The conductivity increase is due to the decrease of the hopping barriers as a result of a greater number of densities of state which was introduced by GN in the PPy matrix. The values of the exponent $(s)$ were calculated from the slope of the curves plotted between $\ln(\sigma(\omega))$ and $\ln(\omega)$, as shown in Figure (8) and are listed in Table(1). The exponent $(s)$ was found to be less than unity, $(0.65-0.96)$, and increased with the increase of the concentration of GN, which represented to correlated Hopping mechanism between polymer chain [12].
Figure 8: Variation of $\sigma_{A.C}$ with angular frequency for pure PPy and PPy/GN Nanocomposites.

| Sample | PPy  | 0.1% | 0.3% | 0.5% | 1% | 3% | 5% |
|--------|------|------|------|------|----|----|----|
| S      | 0.653| 0.720| 0.761| 0.788| 0.703| 0.882| 0.962|

4. Conclusions

In this section we welcome you to include a summary of the end results of your in this work, polypyrrole polymer was prepared from the oxidation of (2ml) pyrrole with (3g) of ferric chloride in aqueous medium. Measurements of optical energy gap were done. The minimum optical energy gap value was (2.1 eV) for pure PPy and decreased with increasing the doping level of GN to became 1.3 eV for 5%wt. All samples have direct energy gap. Measurements of A.C electrical conductivity showed that the conductivity increased by about four orders of magnitude with the increase in frequency and GN concentration.

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Conflict of interest

Authors declare that they have no conflict of interest.

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الخواص البصرية والكهربائية للبولي بيرول والمتراكب النانو بيرول-الكرافين

في هذا العمل، استخدمنا الأكسدة الكيميائية لبلمرة البوليمر المتراكون "بولي بيرول" في درجة حرارة الغرفة وأضفنا جسيمات الكرافين النانوية خلال عملية البلمرة للحصول على المتراكب (PPY-GN). تم استخدام التحلل الطيفي للأشعة فوق البنفسجية في الطول الموجي بين (200-800 نانومتر) وحساب طيف الإستحصال البصري وطيف الإنتشال الكهرومغناطيسي. حيث أوجدت النتائج ارتفاع قيمته و الفجوة الكهرومغناطيسية عند الطول الموجي (280 و 250 نانومتر) عند جسيمات الكرافين النانوية. و عند حساب الفجوة الطاقة أظهرت النتائج ان المراکب النانوي (PPy-GN) كانت (1.516 eV) لتركيز 5wt.%% من الكرافين النانوي. و المراکب النانوي (PPy-GN) كانت (0.0949 eV) للبولي بيرول النقي.

من خلال النتائج يمكن أن يزداد عرض ذيل الفجوة (ΔE) و يقل عند زيادة تركيز جسيمات الكرافين النانوية و زيادة تركيز التوصيل الكهرومغناطيسي (H.C.P). و قد تم حساب ثابت العزل الكهرومغناطيسي في نطاق التردد بين (10^5 Hz-10^7 Hz) و وجدت أن النتائج تتبع الاتجاه الصحيح و يقل بزيادة التردد.