Optical properties and FT-IR spectra of PANI/f-MWCNT thin films

Zain A. Muhammad, Tariq J. Alwan*

Physics Department, College of Education, Al-Mustansiriyah University, Baghdad, Iraq
*) E-mail: tariqjaffer2000@yahoo.com

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Polyaniline (PANI) and PANI/f-MWCNT thin films have been synthesized by the in-situ chemical polymerization method. Ammonium persulfate (NH₄)₂S₂O₈ and hydrochloric acid (HCL) were used as an oxidizing agent and protonic acid dopant, respectively. The f-MWCNT was added to PANI matrix to enhance and modify its optical properties. The films were deposited on glass substrates by dip coating method and its characterizations were done by UV-Vis (Ultra-Violet Visible Spectrophotometer) and FTIR (Fourier transform Spectroscopy) in the region of (650–2500) cm⁻¹. The optical energy gap and optical constants such as the reflective index, the extinction coefficient and others were carried out from the optical measurements in the wavelength range (300-900) nm. The optical results indicate that the prepared films have allowed direct transition and the optical energy gap depends on the different weight percentages of f-MWCNT which was used as a dopant. FTIR spectrum shows several absorption peaks centered at around 1556, 692, 1235, 830, 1450 and 1280 cm⁻¹ which consider the characteristic band peaks of polyaniline.

Keywords: PANI/f-MWCNT thin films, In-situ polymerization method, Optical properties.

1. INTRODUCTION

Due to the possibility of their commercial application in electronic devices, intrinsically conducting polymers have drawn excellent attention in latest years. For centuries, polymeric materials have been regarded as insulators; however, a redox and oxidation reaction called doping has shown that these polymers can display conductive characteristics [1]. The distinction between a semi-conductive polymer and a non-conductive polymer is due to the nature of the chemical bonds along the backbone of the molecule. The σ-bonds or hybrid orbitals which are formed by head-on overlap are usually responsible for the formation of single bonds. The σ-bonds are consisting of electrons that are localized and have no ability to pass along the backbone of molecular; hence a polymer will be an electrical insulator if only contains single bonds. If instead, the polymer has a conjugated system which are formed by alternating single and double bonds then each carbon atom which lies along the backbone of that system will form one unhybridized p-orbitals and three hybridized orbitals. When sp² orbitals overlap, σ-bonds will be formed, also the overlapping of p-orbitals results in π-bonds. No longer, electrons, take part in π-bonds, belong to a certain atom but will be delocalized.
The combining of two p-orbitals leads to two different orbitals, one is the bonding π-molecular orbital which has a lower energy and the other is the antibonding π*-molecular orbital that has a higher energy. The energy gap of polymer is determined by taking the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The energy gap of polymer lies usually in the range (1-4) eV, this range is similar to that of inorganic semiconductors [3]. Because of its easy synthesis technique, low cost monomer, tunable characteristics, and better stability, polyaniline is a promising material as a conductive polymer. There are three distinct types of PANi: leucoemeraldine base (LEB), emeraldine base (EB, partly oxidized) and perennigraniline base (PNB, fully oxidized) polyaniline has been widely researched since the study of an insulator-to-metal shift to the emeraldine salt (ES-conductive) shape after protonation of the emeraldine base(EB) [4]. In applications such as screens, photoelectrode semiconductor coatings, solar cell and chemical sensors, the conductive type of PANI was used [5]. Most composites that composed of CNT and polyaniline are widely studied. These studies suggested that, there is a π-π interaction between graphitic structure of CNTs and aromatic rings of polyaniline. This interaction leads to the electron delocalization that facilitate the motion of electrons and enhance the electrical and optical properties of composites [6]. Multi-walled carbon nanotubes (MWCNTs) are comparatively chemically inert, display outstanding electrical and thermal conductivity, and demonstrate superior mechanical strength and nonlinear optical properties. Due to their improved electronic and optical characteristics, functionalized MWCNT–PANI nanocomposite thin films have recently drawn considerable attention. Because functionalized nanotubes are readily dispersed in organic solvents, the MWCNT dispersion and homogeneity within the polymer composite are enhanced [7].

The aim of this paper is to prepare semiconducting polyaniline PANI and PANI/f-MWCNT thin films using in-situ chemical method at low temperature, which allows us to get thin films with a good quality and to deposit them over large area, and also to study the influence of different weight percentages of f-MWCNT on the optical properties of PANI thin films.

2. EXPERIMENTAL

2.1. Functionalization of MWCNT

One gram of MWCNT was first immersed in 80 ml of a mixture of sulfuric acid and nitric acid (in 3:1 ratio) and placed in the ultrasound bath for two hours after which the mixture was placed under continuous stirring for a full day at 50°C. After that 10 ml of hydrochloric acid in the form of drops was added to the mixture under continuous stirring. In order to neutralize the mixture, ammonia hydroxide was also added to it in the form of drops until the solution is neutralized and this was confirmed using the pH meter. Then the product is centrifuged at a speed 4000 rpm for 15 minutes and filtered using filter paper, and the resulting powder is washed several times in deionized water and then dried at 80 °C for 6 h. The sample was abbreviated as f-MWCNT.

2.2. Prepare PANI and PANI/f-MWCNT Thin films

The PANI and PANI/f-MWCNT thin films was chemically synthesized by in-situ polymerization method, where using aniline monomer and ammonium persulfate (APS) as oxidant agent and hydrochloric acid (HCL) as protonic acid dopant, accordance to a method similar to the described by A. Jabbar 2018 [8]. The different weight percentage of f-MWCNTs (0, 4, 6 and 8 w%) with respect to aniline were used. PANI and PANI/f-MWCNT
fils was deposited on glass slides. The slides are dipped in aniline/HCl solution then the oxidant agent (APS) was added under constant stirring to start the polymerization process, after 30 min, all the slides are removed from a flask. The obtained films were again immersed in aniline/HCl solution, then rinsed with 1 M HCl and acetone, finally left to dry in air at room temperature. The optical measurements of the thin film deposited on glass substrate are calculated from the transmittance and absorbance spectrum at normal incidence over the range (300–900) nm, by using UV-VIS spectrophotometer type (SHIMADZU)(UV-1600/1700 series). SIDCO England series FT-IR spectrometer is used to carry out the infrared analysis of the wavenumber that ranges 650 to 2500 cm\(^{-1}\).

3. RESULTS AND DISCUSSION

Figure 1 shows the UV-VIS spectra in the range of (300-900)nm for a pure PANI and PANI/f-MWCNT thin films. From the spectra one can observe that there are three absorptions bands for each sample. The bands of the pure PANI thin films are located at 350 nm, 444 nm and 788 nm. The absorption peak at around 350 nm is attributed to \(\pi - \pi^*\) transitions, the bands at 444 nm and 788 nm correspond to transitions \(\pi\) to polaron and polaron to \(\pi^*\) respectively [9]. As expected these three bands should appear in the UV-Vis spectrum of the conducting emeraldine salt polymer. From the absorbance spectra it can be seen that the increasing of the weight percentage of f-MWCNT causes the peaks to shift to higher wavelength region, the reason for the band shifting is due to the new excitation energy levels created by f-MWCNT near the band gap of material [10]. Also there is an increase in the absorption magnitude as the weight percentage of the f-MWCNT increase. The obtained absorption bands are in good agreement with that reported in the literature [11].

![Figure 1: The absorbance spectra for a pure PANI and PANI/f-MWCNT thin films](image)

The absorption coefficient \(\alpha\) cm\(^{-1}\) is calculated in the fundamental absorption region using Lambert law [12];

\[
I = I_0 e^{-\alpha t}
\]

(1)

Where \(I_0\) and \(I\) are the intensity of the incident and transmitted light respectively. If \((I/I_0) = T\) then

\[
\alpha = \ln \left( \frac{1}{T} \right) / t
\]

(2)

Where \(T\) is a transmittance and \(t\) is a thickness that has a value of about 200±20 nm for all samples. The absorption coefficient is very important property of a material. The ability of material to absorb light radiations is based on the value of absorption coefficient, also it is
represented a key parameter for designing many optoelectronic components like photovoltaic cells, photodiodes and photo-detectors photo-detectors. Figure 2 shows the variation of the calculated absorption coefficient of the pure PANI and PANI/f-MWCNT as a function of the incident photon energy. It can be seen from Figure 2 the absorption coefficient for all samples is greater than $10^4$ cm$^{-1}$ and this confirms that the type of the transition is the direct allowed transition[13]. Also from curves it is noticed that the absorption coefficient increases with the increase of the weight percentage of the f-MWCNT.

![Figure 2: The variation of $\alpha$ vs. photon energy for PANI and PANI / f-MWCNT thin films](image)

Optical absorption spectra are considered one of the most important tools to compute the optical energy gap ($E_g$) of organic and inorganic semiconductors. Energy gap is of fundamental importance, since the energy gap specifies the electrical conductivity and optical absorption character of the PANI. In many amorphous materials, photon absorption is found to obey the Tauc relation [14], which is of the form:

$$\alpha hv = A (hv - E_g)^n$$

(3)

where $\alpha$ is the absorption coefficient, $hv$ is the photon energy, $E_g$ is the optical band-gap, $A$ is a constant depending on the material's properties and $n$ is a constant which can take various values depending on the type of electronic transition, for the direct and indirect allowed transition $= 1/2$ or 2, respectively. The best fit line is obtained for the direct allowed transition $n= 1/2$.

Figure 3 shows the variation of $(\alpha hv)^2$ with photon energy ($hv$) for direct allowed transition to pure polyaniline and PANI/ f-MWCNT thin films. The optical energy gap are determined from this fig. and listed in Table 1. It can be seen from the Table (1) as the f-MWCNT content increases the optical band gap decreases, from 2.59 eV to 2.45 eV. The reduction in the optical band gap is due to the modification of the polymer structure as result of the interaction of f-MWCNT with polyaniline.[15]
The extinction coefficient is a parameter that determines by how much light intensity will be reduced as light moves a distance $x$ through the medium. The $K_0$ is calculated by the following equation:[16]:

$$K_0 = \frac{\alpha \lambda}{4\pi}$$

(4)

where $\lambda$ is the wavelength of incident rays.

Figure 4 illustrates the variation of extinction coefficient $K_0$ with the photon energy. The behavior of the extinction coefficients of a pure PANI and PANI/f-MWCNT thin films is similar to that of the absorption coefficient since they are related each other by equation (4).
The refractive index is a ratio between the velocity of light in a vacuum to that of light in the medium. Its value can be computed by using the following equation [17]:

\[
n = \left[ \frac{(1+R)^2}{(1-R)^2} - (K_o^2+1) \right]^{1/2} + \frac{(1+R)}{(1-R)}
\]

where \( R \) is a reflectance. Figure 5 demonstrate the variation of the refractive index \( n \) with the photon energy. The refractive index curve of the pure PANI is observed as a concave curve in the range of photon energies (2.1 to 2.6) eV, also it is seen that in this range the higher the weight percentage of the f-MWCNT content, the more flat the curve becomes. This means the value of the refractive index becomes approximately constant in this region.

**Figure 5**: The variation of \( n \) vs. wavelength for PANI and PANI / f-MWCNT thin films

The complex dielectric constant \( \varepsilon \) is the material's ability to polarize, whose expression is given by the following equation [18]:

\[
\varepsilon = (n*)^2 = (n+iK_o)^2
\]

But the complex dielectric constant has two parts as:

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2
\]

Where \( \varepsilon_1 \) and \( \varepsilon_2 \) represent the real and imaginary parts of complex dielectric constant and they are illustrated by the following relations:

\[
\varepsilon_1 = (n^2 - K_o^2)
\]

\[
\varepsilon_2 = 2nK_o
\]

The two parts of the dielectric constant which are varied with photon energy are shown in Figure 6 and 7 for pure PANI and f-MWCNT thin films. As the values of \( K_o^2 \) is small compared to that of \( n^2 \), so the overall variation of \( \varepsilon_1 \) will rely on the \( n^2 \) values, while \( \varepsilon_2 \) is based on the \( K_o^2 \) values that associated with the absorption coefficient variation.
Figure 6: The variation of $\varepsilon_1$ vs. photon energy for PANI and PANI / f-MWCNT thin films.

Figure 7: The variation of $\varepsilon_2$ vs. Photon Energy for PANI and PANI / f-MWCNT thin films.

3.1 FT-IR studies

FTIR spectroscopy is a good selection for both organic and inorganic materials to study the molecular structures and their bonding. The unidentified elements present in the sample can also be identified. FTIR spectra of pure PANI and PANI / f-MWCNT nanocomposites thin films in the region of (650–2500 ) cm$^{-1}$ were illustrated in Fig.(8). The characteristic band peaks for pure polyaniline occurs at 1556, 692, 1235, 830, 1450 and 1280 cm$^{-1}$. The C=C stretch absorption of aromatic compound was obtained at 1556 cm$^{-1}$. The C–Cl stretching peak appears in the band peak 692 cm$^{-1}$ confirmed the Cl- doping of the synthesized polyaniline films in HCL [19]. The peak around 1235 cm$^{-1}$ is assigned to stretching of C–N++ polaron structure that corresponds to the electrically conductive form of doped PANI [20]. The band 832 cm$^{-1}$ corresponding to aromatic ring out of plane deformation vibrations which belongs to C–H deformation in the para–disubstituted ring [21]. The band near 1450 cm$^{-1}$ may be obscured by the aliphatic C–H deformation vibration, finally the band peak 1280 cm$^{-1}$ is attributed to C–H plane bending[22]. In comparison with PANI, the characteristic vibrational
peaks of PANI are also appeared in the PANI/f-MWCNT composites FTIR spectra and the transmission peak intensities of PANI/f-MWCNT composite are lower than pure PANI, indicating the interaction between the f-MWCNT and the polyaniline matrix was taken place [23].

Figure. 8 : FTIR spectra of PANI and PANI / f-MWCNT thin films

3. CONCLUSIONS

The PANI and PANI/f-MWCNT thin films are successfully deposited on a glass substrates by in-situ chemical polymerization method. The optical energy gap is effected by the addition of a f-MWCNT to PANI matrix, it was (2.59 eV) for pure PANI sample and reduced to (2.45 eV) for the f-MWCNT of 8 w %. Also all the other optical constants are varied with the increase of the f-MWCNT. The FTIR measurement revealed the formation of PANI by displaying the characteristic band peaks belongs to it. The width and the intensity of the transmission peaks are impacted by adding the f-MWCNT that indicated the interaction between the f-MWCNT and the polyaniline matrix was taken place. The optical characteristics of all samples indicate that they are an organic semiconductor. According to this, promising results in photovoltaic and optoelectronic devices are expected.

References


