Preparation and Characterization of Polyvinylpyrrolidone/Multi-walled Carbon Nanotubes Nanocomposite hybrid with Graphene

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Abstract

In this work, polyvinylpyrrolidone (PVP), Multi-walled carbon nanotubes (MWCNTs) nanocomposite was prepared and hybrid with Graphene (Gr) by casting method. The morphological and optical properties were investigated. Fourier Transformer-Infrared (FT-IR) indicates the presence of primary distinctive peaks belonging to vibration groups that describe the prepared samples. Scanning Electron Microscopy (SEM) images showed a uniform dispersion of graphene within the PVP-MWCNT nanocomposite. The results of the optical study show decrease in the energy gap with increasing MWCNT and graphene concentration. The absorption coefficient spectra indicate the presence of two absorption peaks at 282 and 287 nm attributed to the π-π* electronic transition which is found in MWCNT and Gr. The energy gap (E_g) has been obtained from the indirect allowed transition. It was found that, E_g decrease with the addition of MWCNTs and Gr content.

1. Introduction

Carbon nanotubes (CNT) have captivated the interest of researchers and scientists since Ijiman discovered them due to their extraordinary optical, electrical, thermal, and mechanical properties. They have a wide range of applications such as supercapacitors [1], transistors [2], Schottky contacts [3], solar cells [4], gas sensors[5]. Graphene (Gr) is a zero-gap semiconductor with a very high electrical conductivity. Its conduction and valance bands intersect at the Dirac points. It's made up of a single atomic layer of sp2-bonded carbon atoms and is structured in a two-dimensional honeycomb lattice. In vacuum, graphene forms an extremely opaque atomic monolayer due to its capacity to absorb around 2.3 percent of white light [6-8]. Polymer composites are most attractive to be used with CNT and Gr, since the result is with interesting properties [9-10]. However, it is so difficult to get homogeneous solution of polymer, CNT and Gr, since Gr is enormous uniform arrangement of carbon atoms connected by covalent bonds; it has a very high melting temperature and is extremely strong. Polyvinylpyrrolidone (PVP) is water soluble and in many polar solvents such as ethanol which made it easy to fabricate. It is good in stable environment and of moderate electrical conductivity which attracts researches for many years especially it has high dielectric strength with good charge storage capacity. The effect of Gr and MWCNT hybrid system on the polymeric composites has been investigated. The results shows an enhancement in the mechanical, electrical, thermal and optical properties comparing to their use individually [11-13].

This hybrid system has many important applications in growing pharmaceutical, biomedical, electronic and optical applications [14,15]. In this work, casting method is used to prepare PVP/MWCNT nanocomposite hybrid with Gr. The morphological and optical properties were emphases.

2. Materials and Methods

PVP was supplied by Sigma-Aldrich with average molecular weight of 64000 gm/mol, Multi-walled carbon nanotubes (MWCNTs, outer diameter 13- 18nm) with length ~1-12 μm, and purity > 99 wt % was purchased from Neutrino. Graphene platelet nanopowder with thickness 608nm and average particle diameter 15µm was supplied by Skyspring nanomaterials Inc. The nanocomposite was prepared in an aqueous suspension using ethanol. In distilled water, a 4mg/mL PVP was dissolved and sonicated with energy >20kHz for 30 min. MWCNT were

prepared, by dissolving in 50 ml of ethanol and stirred for about 2 hours with at room temperature before its stirred with PVP for about 90min. Then Gr powder was added to the nanocomposite during the stirring and sonicated for 90 min. The resulting samples were drop casting on to glass substrates with dimension of (2.5×2.5) cm for characterization.

The structural properties of the samples were investigated using Fourier transformer infrared (FTIR) spectroscopy type- Shimadzu 8400 FTIR spectroscopy. The surface morphology of prepared samples was studied using Field Emission-scanning electron microscope (FESEM), Hitachi S3000H instrument and using the double beam Shimadzu–UV -1800 scanning spectrophotometer in the wave length 200-1100 nm is used to investigate optical properties of obtained samples. The ability to measure the transmission and absorption of thin film is essential for a variety of optical devices applications. The energy gap (E_g) of the samples was determined through Tauc plots. The ratio of the intensity of light absorbed I_A by the sample to the incoming intensity of light is defined as A [16]:

$$A = \frac{I_A}{I_0} \tag{1}$$

Absorption coefficient (α) is given as[17]:

$$\alpha = \frac{2.303A}{d} \tag{2}$$

where d represent sample thickness.

Optical parameters such as absorption coefficient (α), and energy band gap (E_g) were determine using optical measurements of the polymer films. Tauc put the empirical equation   relating optical energy gap and incident photon energy [18]:

$$\alpha h\upsilon = B\,(h\upsilon - E_g)^r \tag{3}$$

where (hυ) is the photon energy, B is a constant and E_g is the band gap between the valance band and the conduction band, and r is the order of the optical transition depending on the nature of electronic transition, which can be take values = 1/2, 3/2, 2 and 3 that represents direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively.

3. Results and discussion

The purpose of FTIR spectroscopy is to examine multi-component functional groups and provide helpful information about the mechanism of interaction and the content of the material phase in a variety of bond types found in all samples. Fig.1a, shows the FTIR spectrum for pure

PVP, Pure MWCNT, and PVP/MWCNT nanocomposites. For PVP, the peaks at 3452.36cm^{-1} corresponds to OH stretching, the peaks at 2954.95 cm^{-1} corresponds to C-H stretching. Peak at 1514.12 cm^{-1} corresponds to characteristic vibration of C=N (pyridine ring). Peaks at 1514.12 cm^{-1} and 1224.80 cm^{-1} represents the characteristic vibration of C=N (pyridine ring) and C-C stretching and/or CH$_2$ deformation, respectively, as it can be seen in table (1). For FTIR spectrum for the PVP/MWCNT nanocomposite, the intensity of the peaks has decreased due to the existance of MWCNT . The broad peak at 3477 cm^{-1} is due to OH stretching vibration of the hydroxyl groups. Also, the peak at 1654.92 cm^{-1} has decreased in intensity and became broader. This exhibits the structural changes of PVP after being filled with MWCNT. The shift of wave number indicates the change in potential energy distribution along the polymeric chain. There is good agreement between these results and those of Alibe[14] and Zidan. [19].

In Fig.(2&3), FTIR spectrum for pure graphene shows a strong and broad peaks at 3473.80 cm^{-1} which correspond to O-H stretching vibration band. 2954.95 cm^{-1} is due to the CH2 streching. The carboxyl C=O stretching band at 1662.84 cm^{-1} shows strong peak, 1427.32 and 1285.44cm^{-1} are corresponding to the C-H deformation vibration band and C-O stretching vibration. The effect of graphene was obvious by its peaks, where the main peaks, with slightly shift, at 3446.79cm^{-1}, 2954.95 cm^{-1}, and 1654.92 cm^{-1} were recognized. The spectrum shows increase in intensity with the presence of graphene.
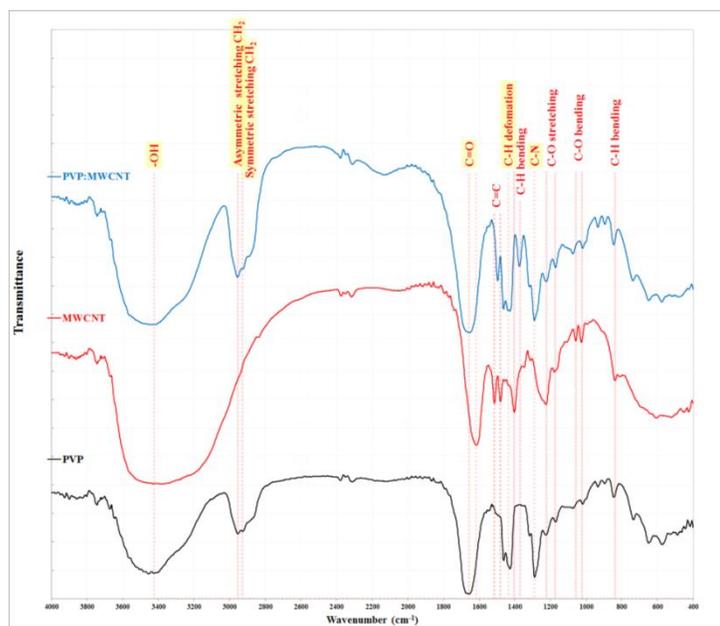

Figure 1: FTIR spectra for a) pure PVP, b)PVP/MWCNT nanocomposite and c) PVP/MWCNT nanocomposite
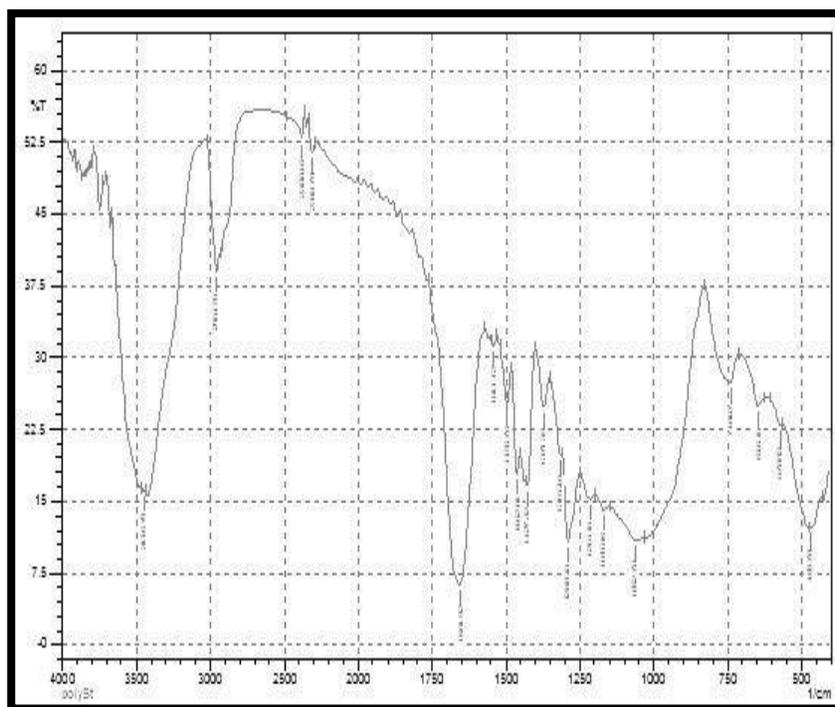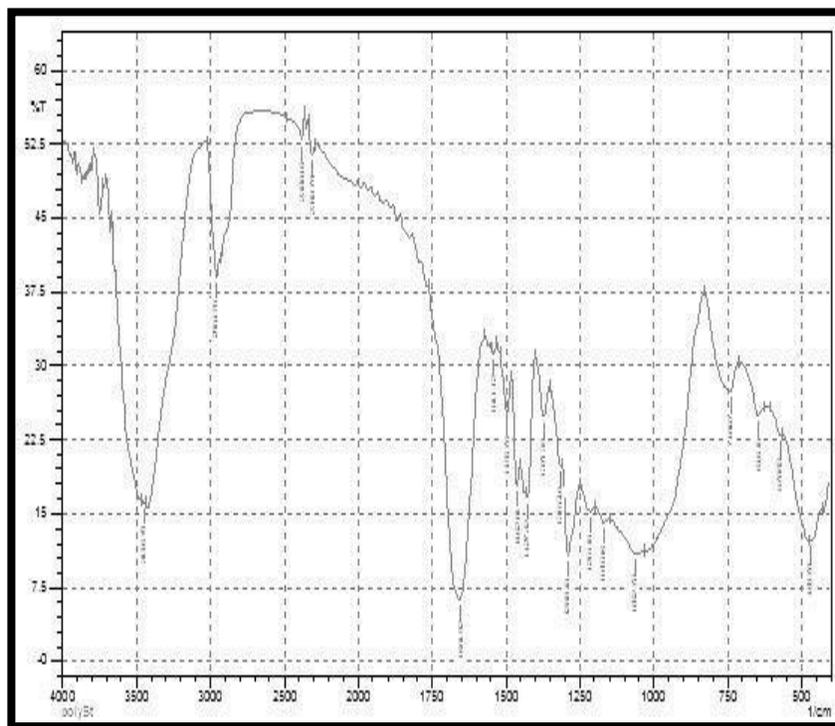
Figure 2: FTIR spectrum of pure graphene

Figure 3: FTIR spectrum for PVP/MWCNTs nanocomposites hybrid with graphene.

Table 1: List of FTIR peaks for all samples

Band Type	PVP	MWCNT	Graphene	PVP/MWCNT nanocomposite	PVP/MWCNT nanocomposite/ Hybrid with Graphene
O-H	3452.36	3403.54	3473.80	3424.76	3446.79
Asymmetric stretching CH2	2953.54	-	2954.95	2955.66	2954.95
Symmetric stretching CH2	2925.94	-		2928.07	
C=O	1660.85	1616.27	1662.84	1658.97	1654.92
C=C	-	1514.39		1494.87	
C=C	-	1480.42		1464.1	
C-H deformation	1427.36	-	1427.32	1428.21	
C-H bending	-	1404.01	-	-	
C-H bending	-	1346.7	-	1374.36	
C-N	1287.26		-	1292.31	
C-O stretching	-	1221.46	1285.44	1225.64	
	-	1172.64		1171.79	
C-O bending	-	1058.02		1071.79	
	-	1024.06		1020.51	
C-H bending	-	839.387		846.154	

FESEM is commonly used to examine the compatibility of various components of a film, as well as to detect phase separations and interfaces. Figure 4 shows the SEM images of pure PVP, PVP-MWCNT nanocomposite and nanocomposite hybrid with Gr samples. it shows the

uniform dispersion of MWCNT/Gr within the PVP matrix [20]. The surface of the PVP shown in Figure 4a is smooth, uniform and no crack can be observed also it tend to agglomerate. In Figure 4b, the PVP/MWCNT nanocomposite show a good compatibility and homogeneous. The uniform dispersion of MWCNT/Gr within the PVP matrix was shown in Figure (4c).
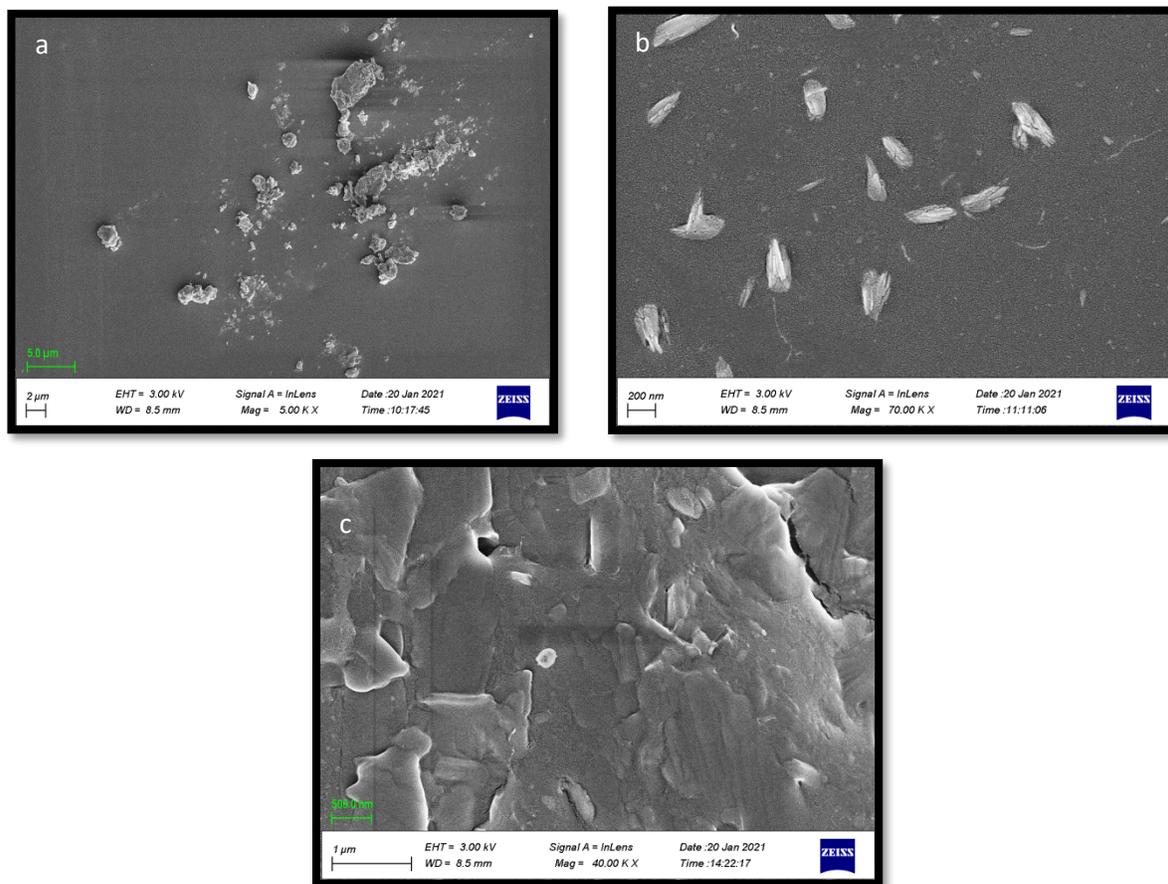

Figure 4: FESEM for (a) pure PVP, (b) PVP-MWCNT nanocomposite and (C) PVP-MWCNT nanocomposite hybrid with grapheme

Figure 5 shows the UV-Visible spectra of all samples. The absorption in the UV-region is more than in the visible region. The absorption peaks where observed at wavelength (280-700) nm. The absorption peaks for MWCNT was around the wavelength 282nm [17] While PVP showed a sharp absorption peak at 287nm which is in agreement with the results of Ahmed [18]. The addition of MWCNT and Gr resulted in a shift in the absorption edge to the lower photon energy sides. The absorption edge is representing the region where an excited electron by an incident light rises from a lower energy state to a higher energy state.
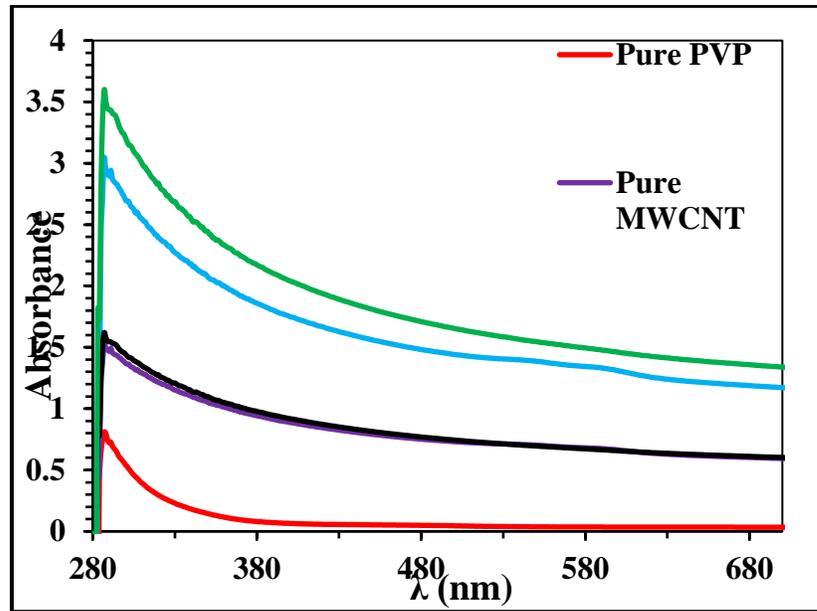
Figure 5: Absorbance spectra of all samples films

Using Tauce relation in Eq. 3, the energy gap E_g was calculated. The E_g is used to correlate the shift in UV-visible spectra's fundamental absorption edge. Table 2 shows the E_g values. By comparing the optical energy gap values of PVP-MWCNT and PVP-MWCNT-Gr nanocomposite with that of the pure samples, a shift towards long wavelengths can be noticed. This can be attributed to the π-π* transition which is found in MWCNT and Gr, which agree with our previous work Estabraq et al. [13]. Figure 6 shows the relation between $(\alpha h\upsilon)^2$ and hυ (which are called Mott plots) for all samples. The straight part of this curve shows that the nature of the transition is indirect allowed. The intercept of the extension of the linear part with the hυ - axis represents the value of the indirect energy gap E_g. Table 1 shows the values of E_g for all samples. The energy gap for PVP has decreased by adding MWCNT to form the nanocomposite. Because of the formation of various polaronic and defect levels, MWCNT alters the electrical structure of the polymeric matrix [17]. The addition of Gr to the nanocomposite cause further decrease in the energy gap which may be attributed to the formation of localized states in the band gap due to compositional disorder.

Absorption coefficient α(υ) and extinction coefficient k were also calculated at 280 nm wavelength for all samples by Eq.2 and 4.

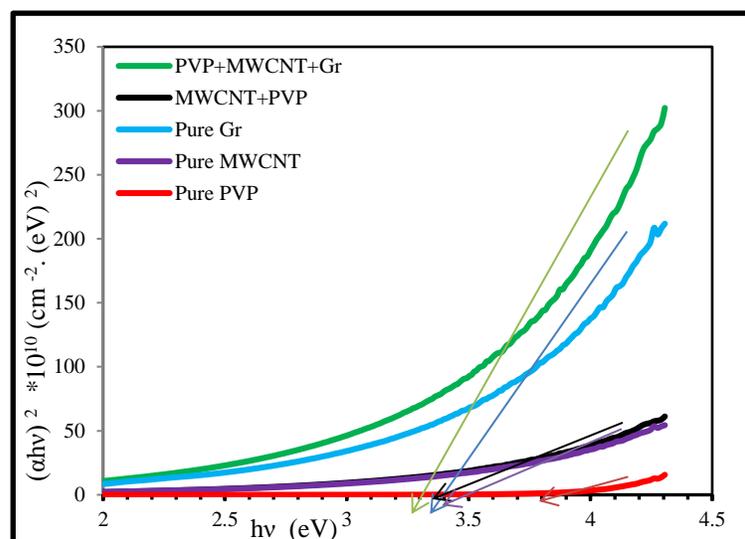$$K=\alpha\lambda/4\pi \qquad\qquad (4)$$

Figure 6: Absorption coefficient versus wavelength for all samples

Table 2 The optical parameters values of all samples

samples	E_g (eV)	K
Pure PVP	4.00	0.019
Pure MWCNT	3.6	0.354
Pure Gr	3.35	0.699
PVP/MWCNT nanocomposite	3.5	0.351
PVP/MWCNT nanocomposite hybrid Gr	3.4	0.780

Conclusions

A casting technique method was employed to prepare PVP /MWCNT nanocomposite hybrid with graphene at room temperature. Their morphological and optical properties were investigated. FTIR analysis indicates the formation of intermolecular interaction between the PVP and MWCNT and Gr. SEM images indicate the homogenous nature of the prepared samples without aggregation. The optical absorption spectra show that the transition was indirect

allowed. The energy gap varied from 4.00 to 3.4eV. Absorption coefficient and extinction coefficient were calculated at 280nm.

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تحضير وتوصيف البولي فينيل بيروليدون / الأنابيب النانوية الكربونية متعددة الجدران الهجين النانوي المركب مع الجرافين

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المستخلص

في هذا العمل، تم تحضير مركب البولي فينيل بيروليدون مع أنابيب الكاربون النانوية متعددة الجدران وتهجينه باستخدام الجرافين باستخدام طريقة الصب. تم فحص الخصائص المورفولوجية والبصرية. يشير فحص الاشعه تحت الحمراء إلى وجود قمم مميزة أولية تنتمي إلى مجموعات الاهتزاز التي تصف العينات المعدة. أظهرت صور الفحص المجهري الإلكتروني تشتتًا موحدًا للجرافين داخل المركب النانوي المتكون من البوليمر وانابيب الكاربون النانويه. كما وأظهرت نتائج الدراسة الضوئية انخفاضًا في فجوة الطاقة مع زيادة تركيز انابيب الكاربون النانويه وتركيز الجرافين. تشير أطياف معامل الامتصاص إلى وجود قمتي امتصاص عند 282 و 287 نانومتر تعزى إلى الانتقال الإلكتروني * π-π الموجوده في أنابيب الكاربون النانوية متعددة الجدران والكرافين. وجد ان فجوة الطاقه من الانتقال غير المباشر المسموح به ينخفض مع إضافة محتوى من أنابيب الكاربون النانوية متعددة الجدران والكرافين.