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Impact of PEDOT:PSS Concentration and Heat Treated on Compositional and Some Optical Properties for Graphene Oxide Thin Films

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Abstract

In this study the as-deposited and heat treated at 423K of conductive blende graphene oxide (GO) / poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) thin films was prepared with different PEDOT:PSS concentration (0, 0.25, 0.5, 0.75 and 1.0)wt% on pre-cleaned glass substrate by spin coating technique. The energy dispersive X-ray Analysis (EDX) show the existence of higher amount of carbon and oxygen related to hydroxyl and carbonyl groups. X-ray diffraction (XRD) analysis of the as-deposited and annealed GO/PEDOT:PSS thin films blend indicated that the film prepared show broad peak around 8.24 corresponding to the (001) level refers to GO, this peak shifted to the lower 2θ with increasing PEDOT:PSS concentration. These results of Fourier transform infrared spectroscopy (FTIR) support the EDX measurement and confirm all the bonds of mixed compounds before and after annealing process. UV-visible spectra of the GO was registered for investigation the peak at ~ 224 nm along with the shoulder at ~ 260 nm. After blending, there are a small shifts in the peaks locations toward the red shift wavelength with increase the concentrations of PEDOT:PSS, while after heat the peaks locations shift toward the blue shift wavelength.

Keywords: GO, PEDOT:PSS, blending, thin films.

تأثير تركيز PEDOT: PSS والمعالجة الحرارية على التركيب وبعض الخصائص البصرية للأغشية الرقيقة من أكسيد الجرافين

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الخلاصة

في هذه الدراسة ، تم تحضير الأغشية الرقيقة التي تم ترسيبها والمعالجة بالحرارة عند 423 كلفن من أكسيد الجرافين الموصل / (GO) بولي (3،4-إيثيلين ديوكسي ثيوفين) - بولي (ستيرين سلفونات) (PEDOT: PSS) بتركيز مختلف (0 ، 0.25 ، 0.5 ، 0.75 و 1.0) بالوزن٪ على الركيزة الزجاجية التي تم تنظيفها مسبقاً بتقنية الطلاء الدوراني. يوضح تحليل الأشعة السينية المشتمت للطاقة (EDX) وجود كمية أكبر من الكربون والأكسجين المرتبطة بمجموعات الهيدروكسيل والكربونيل. تحليل حيود الأشعة السينية (XRD) لمزيج GO/ PEDOT:PSS المودع والمصلب: أشار مزيج الأفلام الرقيقة إلى أن الفيلم المعد يظهر ذروة واسعة حول 8.24 المقابل للمستوى (001) يشير إلى GO، تحولت هذه الذروة إلى الأسفل 2 مع زيادة تركيز PEDOT: PSS.

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تدعم نتائج التحليل الطيفي بالأشعة تحت الحمراء لتحويل فورييه (FTIR) قياس EDX وتؤكد جميع روابط المركبات المختلطة قبل وبعد عملية التلدين. تم تسجيل أطياف GO المرئية للأشعة فوق البنفسجية للتحقيق في الذروة عند حوالي 224 نانومتر مع الكتف عند 260 نانومتر. بعد المزج ، هناك تحولات صغيرة في مواقع القمم باتجاه الطول الموجي للإزاحة الحمراء مع زيادة تركيزات PEDOT: PSS ، بينما بعد الحرارة تتحول مواقع القمم نحو الطول الموجي للإزاحة الزرقاء .

Introduction

Conductive polymers (CPs) are organic polymers that differ from typical polymers because they can conduct electricity through their conjugated structures, which consist of double (π) bonds and single (σ) bonds along the CP chains [1]. CPs have sp^2 hybridization in their backbones, in which the p-orbital in each atom is orthogonal to the plane of the polymer chain but parallel to each other, allowing for electron delocalization lengthways the polymer chains[2,3].

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is promising materials because of their unique optical property, high conductivity, light weight, low cost, high thermal stability, flexibility and excellent process ability in industrial manufacturing [4]. PEDOT:PSS has a lower electrical conductivity than the other conductive polymers or metal oxides[5].

Carbon compounds and their derivatives as well as the conductive polymers (CPs) and other which have a sp^2 hybridization with conjugated structures of double (π) bonds and single (σ) bonds along the carbon atoms chain represent an organic semiconductor materials. They combine between the semiconductor behavior and the mechanical properties of organic materials[1,6].

Many applications like solar cells and LEDs searching for materials are optically active and preferably direct electronic band gap, graphene has semi-metallic nature greatly limits its utilization in a number of these applications, therefore, the adding of functionalized groups like a carboxyl group (-COO-) and hydroxyl (OH-) to graphene has been demonstrated experimentally to effect such an electronic modification and get a compound which is name graphene oxide[7]. GO optical properties arise from the band gap that is opened in graphene due to such derivatization. This material that exhibits fluorescence across the band gap in the visible/NIR (near infrared) region of the electromagnetic spectrum and inherits high transparency and significant tensile strength from graphene platform. Also, unlike graphene GO is water soluble which allows its direct deposition from aqueous suspension for device applications. These eminent properties make GO suitable for optoelectronics and bio imaging applications[8]. GO is flexible, high-processing, and low-cost material with impressive consumer electronics potential applications[9].

In this work, we examined two promising materials graphene oxide and poly (3,4-ethylenedioxythiophene) / polystyrenesulfonate (PEDOT:PSS) to understand the role of PEDOT:PSS concentration in GO matrix is crucial to simplify the film manufacture process. we report comprehensive investigation of the effect of PEDOT: PSS on the composition and some optical properties of the nanocomposite.

Experimental part

The materials that are used to prepare the blend; graphene oxide dissolved in water (1mg/ml) is purchased from Nano scale company and PEDOT:PSS also dissolved in water (1.3mg/ml) is purchased from Sigma Aldrich and used without further purification.

The GO/ PEDOT:PSS blend was prepared using different mixing weight ratios of GO and PEDOT:PSS (1/0,0.25,0.5,0.75and1) and mixing them by magnetic stirrer for 3h at room temperature to get a homogenous solution.

Spin-coating technique is used to deposited GO/ PEDOT:PSS thin films, a small amount of a solution is dispensed on the glass substrate with speed of 2000rpm, then the film was left to dry for one day in room temperature to form solid films. The required thickness of the respective blended films can be controlled by the spin speed[10].

After films preparation, the annealing treatment under vacuum was done with temperature of 423K for 1h. Composition measurements for as-deposited and annealed GO/PEDOT:PSS thin films were done using energy dispersive X-ray Analysis (EDX) analysis to know the element concentration of materials. Using type TESCAN-Mira III scanning electron microscope, provides topographical and elemental information at resolution (1 nm at 30 keV and 2 nm at 1 keV) is possible with certain types of specimens.

Fourier-transform infrared spectroscopy (FTIR) was performed by Thermo Scientific™ Nicolet™ iN™10 Infrared Microscope over the range of 400-4000 cm^{-1} with resolution 4 of the spectra found at room temperature and recorded in the transmittance mode.

The mixture dispersions were coated on a quartz substrate and analyzed by UV–visible spectrophotometer (Japanese company (Shimadzu)) and also deposited and thermoplastic in order to assess the effect of PEDOT:PSS concentration on the absorption film. The ultraviolet–visible absorption spectra were recorded in the wavelength range 200–400 nm at room temperature.

Results and discussion

EDX showing information about the elemental composition of surface of GO/PEDOT:PSS thin films which prepared by spin coated on glass in room temperature and annealed at ($T_a=423\text{K}$) GO/PEDOT:PSS thin film. From Table 1 (a), GO thin film shows the existence of higher amount of oxygen and carbon related to hydroxyl and carbonyl groups, which confirms that the membrane contains GO to its surface. Adding the polymer, contributes to it causes a decrease in the carbon percentage, and on the contrary, the oxygen and sulfur percentage increase. The effect of the temperature was clear on the carbon percentage as it increased after adding the polymer, and the oxygen and sulfur percentage decreased. The percentage presence of normal concentration is given in Table1 (b).

Table 1-Elements weight% composition for GO/PEDOT:PSS thin films (a) as-deposited (b) annealed films

(a) Weight%			
GO/PEDOT:PSS concentration	C	O	S
1/0	25.25	74.75	0
1/0.25	13.14	86.04	0.82
1/0.5	15.41	82.72	1.87
1/0.75	26.1	67.4	6.5
1/1	16.63	81.80	1.57
b Weight%			
GO/PEDOT:PSS concentration	C	O	S
1/0	10.98	89.02	0
1/0.25	13.39	85.77	0.84
1/0.5	25.86	70.99	3.15
1/0.75	25.5	67.8	1.62
1/1	15.02	83.36	1.62

Figure-1 show the X-ray diffraction patterns of the as-deposited GO/PEDOT:PSS thin films which prepared by solution process using spin coating technique. The prepared XRD pattern

of GO shows a distinct broad peak around 8.24° corresponding to the (001) plane and another, more broad peak around 25° may be due to the amorphous glass substrate [20].

The adding of PEDOT:PSS with different concentrations (0.25, 0.5, 0.75 and 1) wt% cause the shifting in the characterized peak of GO toward the lower 2θ . This result indicate that the effect of PEDOT:PSS on the GO structure may be due to form of thin layer on the GO sheets and down shifts the peak to lower 2θ representing the very thin nature of the polymer layers during the formation of the self-assembled ordered structure of PEDOT:PSS. Also, the increase in PEDOT:PSS concentration results in an amorphous composite because the excess polymer content interacts with itself, which reduces the graphene oxide characteristic peak and makes it difficult to determine the inter layer distance [20].

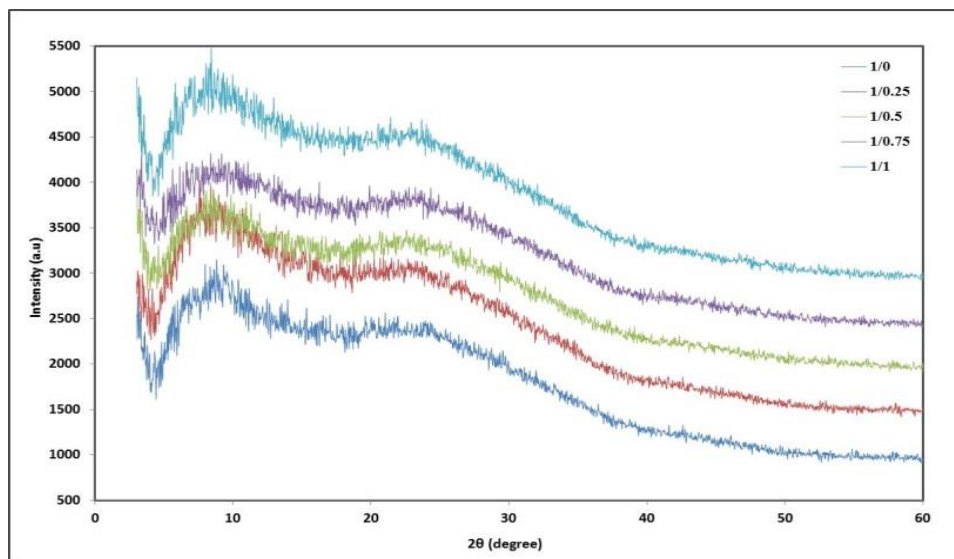


Figure 1-XRD pattern of as-deposited blend GO/PEDOT:PSS thin films

Figure 2(a&b) shows the FTIR patterns in the range $400-4000\text{ cm}^{-1}$ for GO/ PEDOT:PSS nanocomposite blend thin films deposited on glass substrate. The infrared spectrum of GO two distinct bands at 1634 and 1540 cm^{-1} , which corresponded to C=O (carboxyl) and C=C skeleton stretching vibrations, respectively. A wide band around 3400 cm^{-1} indicates stretching vibration of surface hydroxyls and water absorption[11,12].

After blending, the peaks at 614 and 694 cm^{-1} can be assigned to the C–S bond of the thiophene ring in PEDOT. The bands at 1200 , 1095 , and 1034 cm^{-1} are attributed to stretching modes of the alkylendioxy group. Furthermore, a peak appears from the C–H stretching vibration at 2912 cm^{-1} . These peaks have been identified at 1409 cm^{-1} , 1042 cm^{-1} and 1018 cm^{-1} and were associated with the S=O links. Furthermore, two new bands began to appear at 1173 cm^{-1} and 1124 cm^{-1} , increasing with PEDOT:PSS content due to the SO_3 stretching bands of the PSS structure. In addition, this increase in concentration also resulted in an increase the ratio of the $\nu(\text{C–O})$ bonds with respect the C=O ones, since the first ones widespread presence in respect the C=O ones, as shown in Figure 2(a), since the first ones had a pervasive presence in the PEDOT structure. These results are in a agreement with that found by other researchers [13-16]. All investigated bonds listed in Table (2).

Figure 2(b) shows the FTIR patterns for annealed GO/PEDOT:PSS blend thin films at temperatures 423 K . One can see that most of the peaks experienced a slight change in energy bonds with annealing temperature, which demonstrates the increasing atoms packing with annealing. The annealing process is expected to cause residual water removal enabling changes to the bonds of GO and PEDOT:PSS films which already dissolved in water before preparing the films. The evaporation of remaining water is actually sets in around 353 K and

reaches a maximum around 393K as showed from mass spectrometry experiments. Around 423K water have almost completely evaporated from the film.

Also, this figure indicates that the peaks for O-H, in general, decrease with annealing temperature. While the peaks corresponding to C=C aromatic bond with increasing concentration of the PEDOT: PSS.

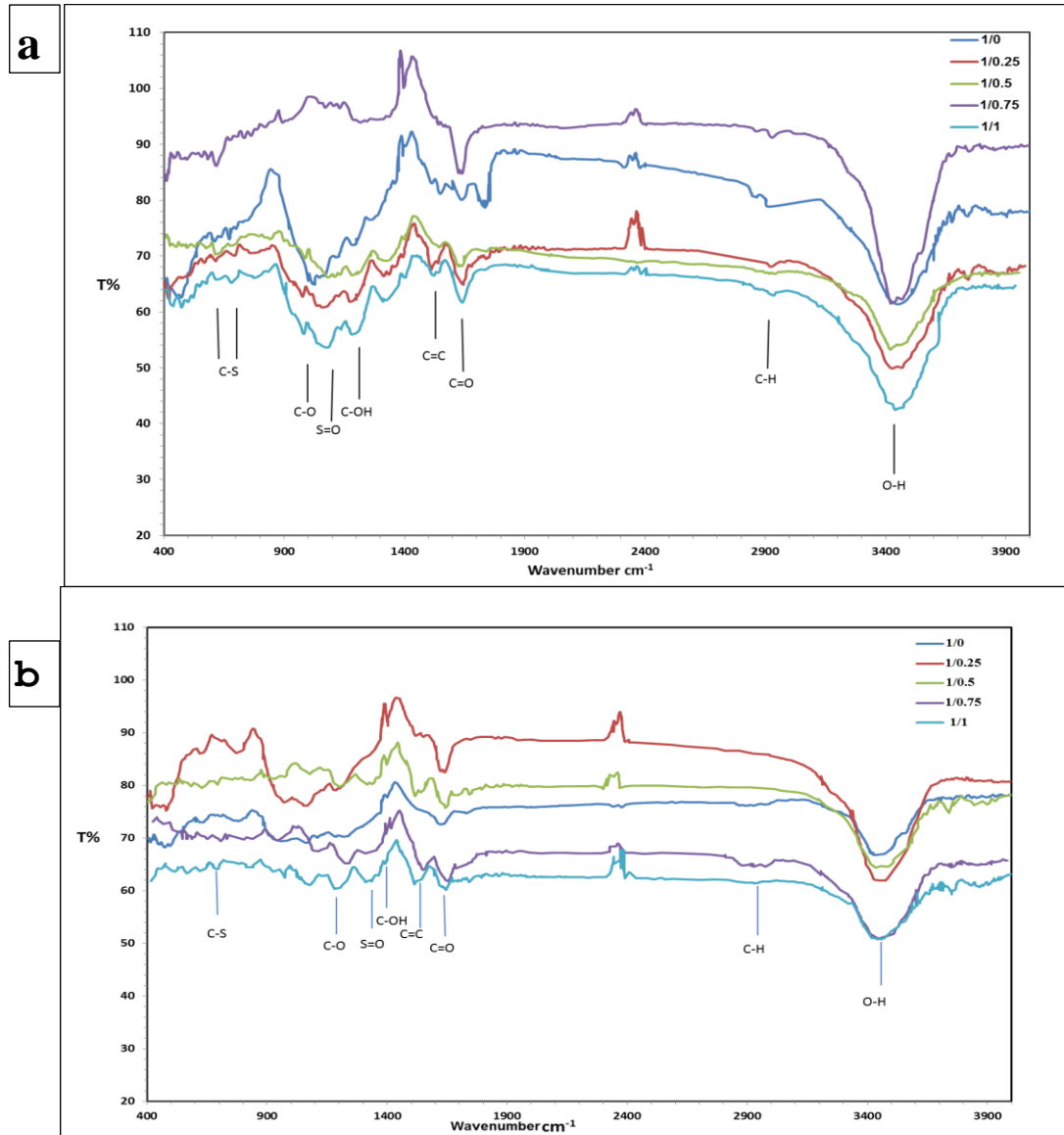


Figure 2- FTIR for GO/ PEDOT: PSS thin films (a)As-deposited (b)annealing

Table 2-FTIR bond for GO/ PEDOT: PSS thin films

Bond type								
GO/PEDOT:PSS Concentration	C-S	C-O	S=O	C-OH	C=C	C=O	C-H	O-H
1/0	-	1000	-	1175	1540	1634	2912	3442
1/0.25	614 694	967	1044	1167	1504	1616	2907	3429
1/0.5	607 668	979	1060	1166	1536	1615	2912	3456
1/0.75	607 691	892	1059	1171	1519	1624	2916	3465
1/1	607 672	975	1064	1171	1507	1624	2911	3463

The absorption for as deposited and heat treatment GO/ PEDOT:PSS thin films on quartz substrate, by spin coating were shown in Figure 3(a&b). The absorbance spectrum of GO was recorded to note the peak at ~ 224 nm along with a shoulder at ~ 260 nm, corresponding to $\pi-\pi^*$ transition of C=C and $n\rightarrow\pi^*$ transition of the C=O bonds in sp^3 hybrid regions, respectively[17,18]. The absorbance peak of PEDOT:PSS appeared nearly 227 nm, which corresponded to $\pi-\pi^*$ transmission of thiophene[19].

After mixing GO with different PEDOT:PSS concentrations as deposited and annealing show that the variations was non asymmetric in absorbance intensity, the higher absorbance was at 0.5 and 1.0 concentrations whereas the lower absorbance in concentrations(0.25,0.75). In general, there are small shifts in the peaks location toward the red shift wavelength with increasing in concentrations of PEDOT:PSS before and after heat affect the peaks locations shifts toward the blue shift wavelength. This shifting may be due to the increase in surface area relative to volume.

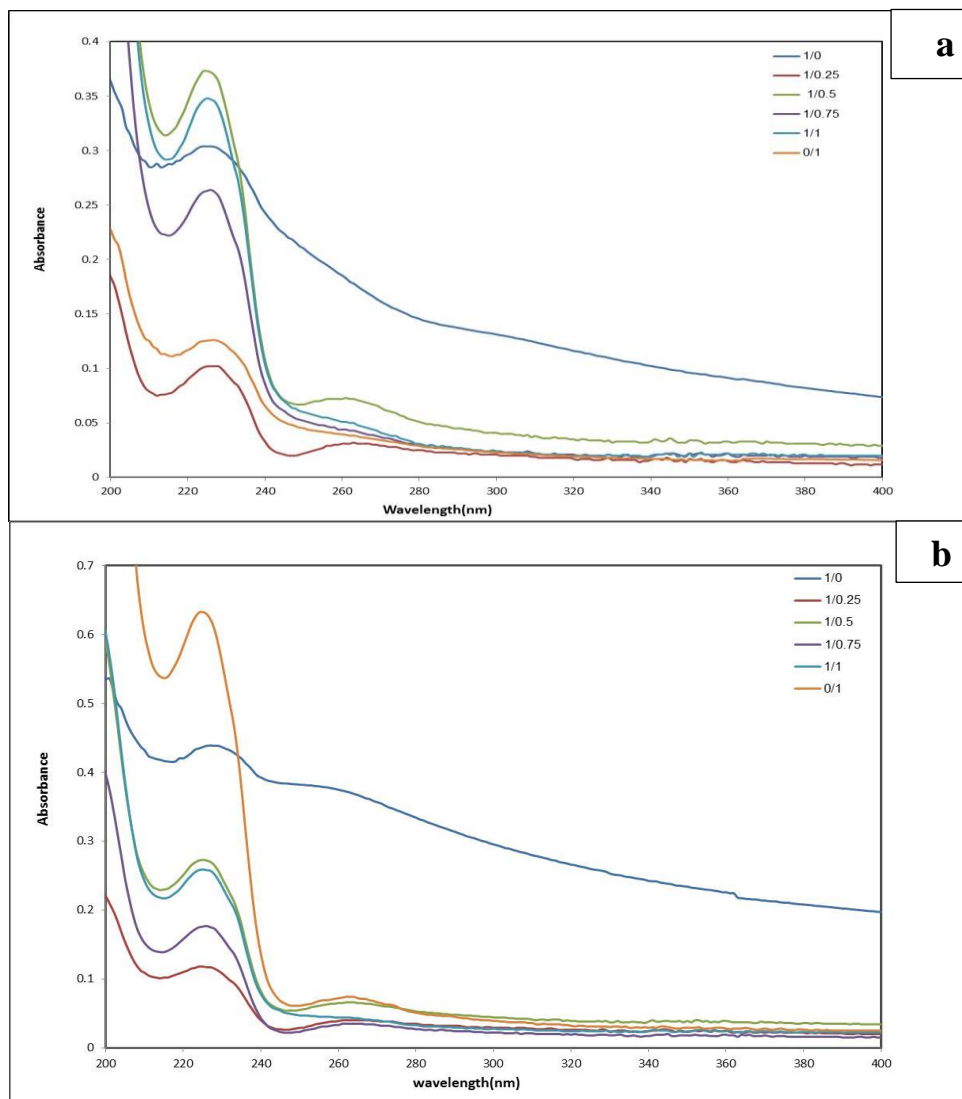


Figure 3-The absorbance spectra of (GO/ PEDOT:PSS) blend thin film (a)As-deposited (b)annealing

Figure-4 shows the variation of $(\alpha hv)^2$ versus photon energy (hv) of incident radiation for as deposited and annealed GO/ PEDOT:PSS thin films. The values of energy gap (E_g) are determined using Tauc equation to find transition type by plotting $(\alpha hv)^r$ where $r=1/2$ versus photon energy (hv) selecting the optimum linear part intersect the hv axis for indirect

transition. The energy gap of GO is 4.83 eV and PEDOT:PSS is 5.11 eV. After blending, the energy gap increases non-systematic with increasing concentration of PEDOT:PSS. After heat treatment, the energy gap also increases non-systematic, as shown in Table (3).

Table 3- The optical indirect energy gaps of (GO/PEDOT:PSS) blend thin film at As-deposited and annealing temperatures

GO/ PEDOT:PSS Concentration	Eg (eV)	
	As-deposited	Annealing
1/0	4.83	4.58
1/0.25	5.16	5.17
1/0.5	5.18	5.16
1/0.75	5.17	5.20
1/1	5.19	5.19
0/1	5.11	5.15

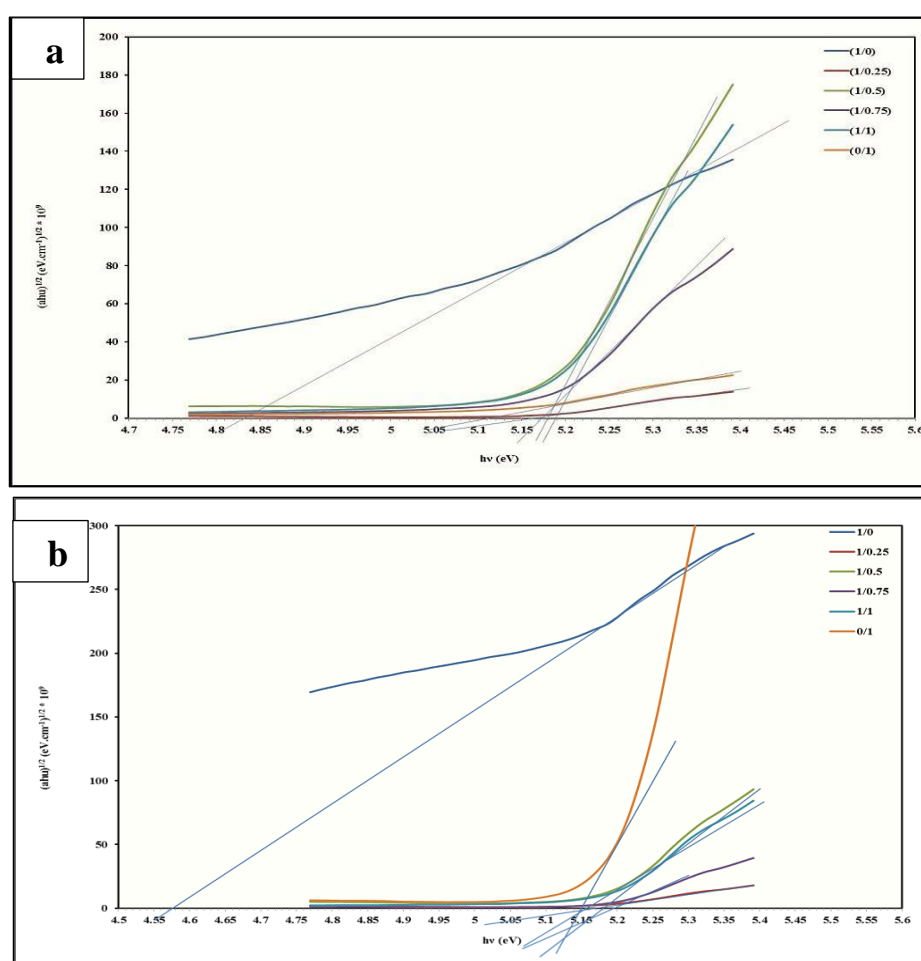


Figure 4- $(\alpha h\nu)^2$ versus photon energy of incident radiation for:(a) as-deposited (b)annealed blend (GO/PEDOT:PSS) thin film

Conclusions

The GO/PEDOT:PSS nanocomposite thin film was successfully prepared using spin coating technique. EDX measurement confirm the thermal stability of GO and PEDOT:PSS by indicating the same elements after annealing. XRD patterns confirm the immobilized of PEDOT:PSS on GO sheets by take the former the orientation of GO in all prepared films, also the increasing of PEDOT:PSS concentration results in an amorphous composite, suggesting the complete loss of the crystalline order perpendicular to the graphitic planes. FTIR measurement support the EDX measurement of thermal stability of two materials. The effect

of adding PEDOT:PSS to GO was clear in UV-Vis measurement by indicating the shift in absorption peaks of prepared samples. The indirect energy gap increases non-systematic with adding PEDOT:PSS.

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