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Structural and Morphological Properties of As-Deposited and Heat Treated Blended Graphene Oxide / Poly(3,4-Ethylenedioxythiophene)-Poly(Styrenesulfonate) Thin Films

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Abstract

In this study the as-deposited and heat treated at 423K of conductive blend 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)w/w on pre-cleaned glass substrate by spin coater. The XRD analysis indicate the existence of the preffered peak (001) of GO around 2θ=8.24° which is domain in all GO/ PEDOT:PSS films characterized for GO, this result approve the good quality of the PEDOT:PSS dispersion in GO, this peak shifted to the lower 2θ with increasing PEDOT:PSS concentration and after annealing process. The scanning electron microscopy (SEM) images and atomic force microscopy (AFM) clearly show the GO flakes and go to disappear with increasing the PEDOT:PSS concentration.

Keywords: Organic semiconductor, Go, PEDOT:PSS, Structural and Morphological

الخصائص الهيكلية والمورفولوجية لأكسيد الجرافين المخلوط والمُعالج حرارياً / بولي (3،4-إيثيلين ديوكسي ثيوفين) – بولي (ستيرين سلفونات) الأغشية الرقيقة

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الخلاصة

في هذه الدراسة ، تم تحضير الأغشية الرقيقة التي تم ترسيبها والمعالجة بالحرارة عند 423 كلفن من مزيج الموصل من أكسيد الجرافين / (GO) بولي (3،4-إيثيلين ديوكسي ثيوفين) – بولي (ستايرين سلفونات ((PEDOT: PSS)بتركيز PEDOT: PSS مختلف (0 ، 0.25 ، 0.5 ، 0.75 و 1) % / % على طبقة زجاجية مُنظَّفة مسبقًا بواسطة طبقة طلاء بالدوران. يشير تحليل XRD إلى وجود الذروة المفضلة (001) من GO حوالي 2 8.24 = θدرجة وهو مجال في جميع أفلام GO / PEDOT: PSS المميزة لـ GO ، وهذه النتيجة توافق على الجودة الجيدة لتشتت PEDOT: PSS في GO ، تحولت هذه الذروة إلى أدنى 2 θ مع زيادة تركيز PEDOT: PSS وبعد عملية التلدين. تُظهر صور الفحص المجهري الإلكتروني (SEM) والفحص المجهري للقوة الذرية (AFM) بوضوح رقائق GO وتختفي مع زيادة تركيز PEDOT: PSS.

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Introduction

Through those past few periods, natural semiconductors need been contemplated extensively, because of their provision over electronic units Similarly as an aftereffect from claiming moving forward the execution about gadgets and modifying those properties of the charge transfer. In 2016, On 2016, propelled Toward inorganic semiconductors, Schwarze et al. Primary news person that band structure building could a chance to be attained for Organic semiconductors Toward blending Organic semiconductors, start an advanced entryway to planning of natural semiconductors. Understanding of the connection between mix ratio and charge transport of devices is imperative for more improvement of organic semiconductors. Those impacts about blending on the charge transfer properties of organic semiconductors can be quite complex [1].

Organic semiconductors are a category of organic materials with semiconductor properties [2], which contain chains of connected carbon atoms (C), either as closed benzene rings (oligomers) or extended chains (normally indicate to as "backbone") of links bonds in polymers [3]. Conducting polymers can be softened and cured from solution, which facilitates the manufacturing procedure. Also, At water may be utilized Similarly as a solvent, those methodology is basic and environmentaly cordial[4].

The conductive polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was discovered 34 years ago and is currently among the most effective conductive polymers commercially offered[4]. PEDOT:PSS is a solution-treatable conductive polymer that provides high transparency, flexibility, low fabrication cost, high thermal stability and compatibility with aqueous solution-built sedimentation procedures [5].

Graphene oxide (GO) have hydroxyl (–OH), carboxyl (C=O) and epoxide functional groups. Hence, it can easily be dissolved into polar solvents like water. These combinations make GO it extremely hydrophilic, nd mixed water molecules tend to appear in the interlayer voids even after lengthy drying [6]. GO is high processable, low-cost and flexible material with remarkable potential applications for consumer electronics [7]. Altering the wettability of the surface restores the homogeneousness of the PEDOT: PSS top level while the incidence of GO restores and expands the electrical conductivity of the film [7-9].

The π-π interactions between GO and PEDOT: PSS promote the form of a tightly coated polymeric layer on the surface of graphene oxide, therefore, PEDOT: PSS was able to prevalent within the well stacked and exfoliated GO structure, resulting in the formation of a thin polymer layer on the graphene oxide layers. Figure 1 illustrates the different types of interactions between GO and PEDOT: PSS [10].

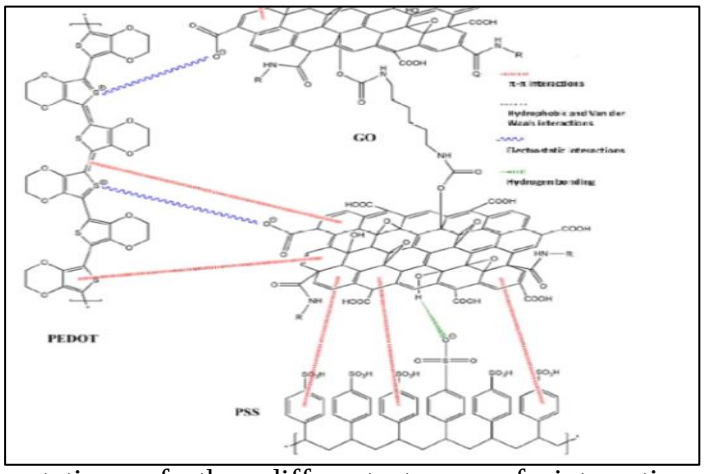


Figure 1-Representation of the different types of interactions between GO and PEDOT:PSS[10].

The understanding the role of PEDOT:PSS in GO matrix is crucial to simplify the film manufacture process as well as to develop device presentation. In this work, we report a detailed investigation of the effect of PEDOT: PSS on the morphological and morphology properties of the nanocomposite.

Experimental

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

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

Spin-coating technique is used to deposite 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.

After films preaparation, the annealing treatment was done with temperature of 423K for 1h. The structure of the GO/ PEDOT:PSS thin films has been analysis and record the intensity as a function of Bragg angle using X–ray diffractometric system Philips-pw1730, Netherlands, Step size = 0.05deg Time per steps = 1s, W.L.=1.54. The radiation source was Cu (K_α) with wave length(λ)= 1.5405Å, the voltage was 40 kV and the current was 30.0 mA. The scanning angle 2θ was varied in the range of (3^o-60^o) with speed 5.0000(degree /min) with preset time = 0.24 (sec).

W.L Bragg was able to deduce his law which stands on the basis that the difference in path between two scattered rays of the same phase equals to whole numbers of X-ray wavelength, and it can be written as [11].

$$n\,\lambda = 2\,d\,\sin\,\Theta_B \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where Θ_B: Bragg's angel, λ: wavelength in (nm), d: inter-planer spacing, n: spectrum order (n = 1, 2, 3 …).

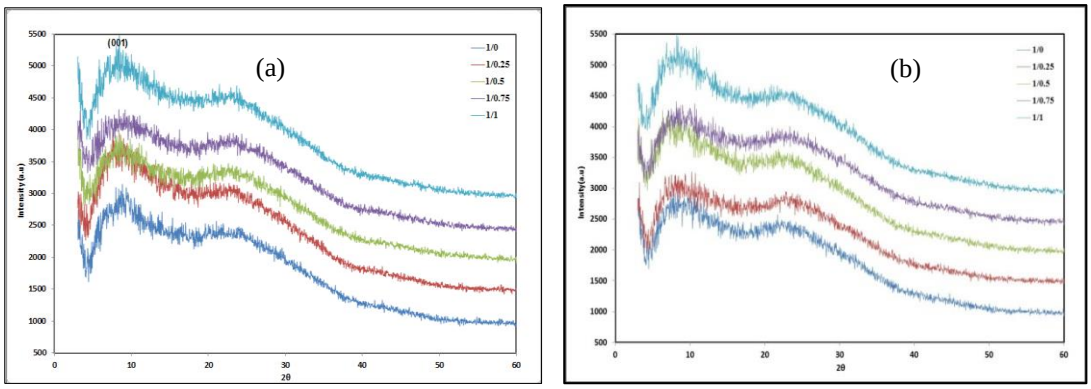
Surface morphological measurements for as-deposited and annealed GO/ PEDOT:PSS thin films were done using Bruker- icon America. AFM micrographs can provide information about roughness and dimensions surface grain size, also 2D and 3D images for all studied samples were obtained**.**

Field Emission Scanning Electron Microscope (FESEM) and energy dispersive X-ray Analysis (EDX) analysis for as-deposited and heat treated thin films used to know the surface morphology and element concentration of materials. type using using 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.

Results and Discussion

Figure 2(a & b) show the X-ray diffraction patterns of the as-deposited and heat treated 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) level. The adding of PEDOT:PSS with different concentrations (0.25, 0.5,0.75,1)w% cause the shifting in the characterized peak of Go toward the lower 2θ, this resut indicate the effect of PEDOT:PSS on the GO structure may be due to the thin layer shapes on the GO sheets and the transfer of the peak to the bottom 2θ representing the very thin nature of the polymer layers during the formation of the self-assembled ordered structure. Also the increasing of PEDOT:PSS concentration results in an amorphous composite beacause the excess polymer content interacts with itself, which decrease the GO characteristic peak and makes it hard to determine the inter sheet distance[12]. The effect of annealing was clear in all prepared film as shown in Figure 2(b), one can observe the more

broadding and decrease in intensity in characterized peak of GO due to the increase in amorphousity which indicate the more intraction between the GO and PEDOT:PSS.

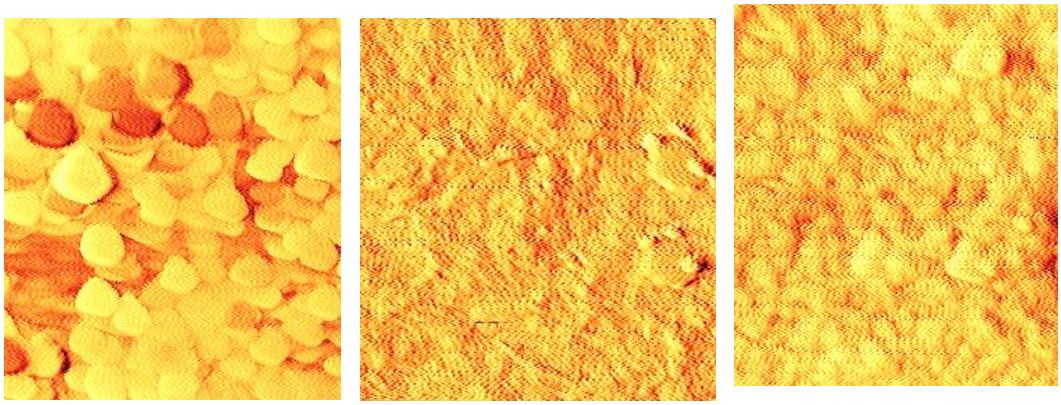


Figures 2-XRD pattern of GO/ PEDOT:PSS Thin Films :(a)as-deposited (b)annealing.

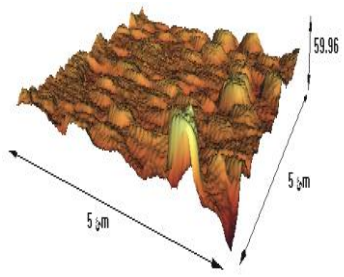
It is clearly from AFM images in Figure 3 displaying adherent, uniformly distributed and wrinkle free sheets od GO in all the cases as well as a good dispersion between the GO and PEDOT:PSS. The thickness profiles are also estimated in all the AFM images, the thickness of the GO sheets on glass were found to be around (5-8)nm and the thickness increase with increasing the PEDOT:PSS concentration while it decrease after annealing process.

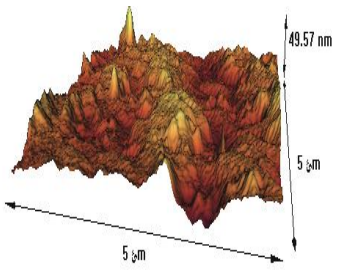
The average diameter or the length of graphene oxide sheets can predictable from 2D-AFM images in Figure 3, it is found that the length of GO increase after adding the PEDOT:PSS and this may be due to the latter cover the GO sheet, but the behavior was unsystematic with increasing the PEDOT:PSS concentration because of the agglomeration of the polymer with increasing the concentration [12]. After annealing treatment the change in average diameter of GO also was unsystematic behavior as shown in Table 1.

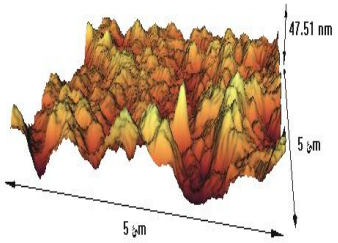
The morphology of GO thin films affected distinctly by loading the PEDOT:PSS which is clearly noticed after measuring the rout mean square roughness ($R_{r.m.s}$) from AFM and also one can see that from 3D-AFM images. Table 1 shows the decrease in ($R_{r.m.s}$) after blended with PEDOT:PSS of (0.25 and 0.5)w% concentration and this expected result because the PEDOT:PSS which cover the GO characterized by low roughness, while it increase with increasing the PEDOT:PSS concentration up to (1)w%. this increase have the same explanation as in average diameter due to agglomeration of PEDOT:PSS. In general the heat treatment leads to decreasing in ($R_{r.m.s}$) for all samples which is induced by water removal at high temperature [13].

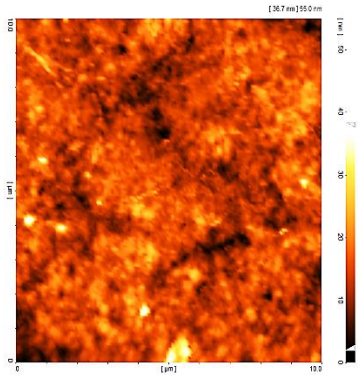


2D(1/0) **2D(1/0.25)** **2D(1/0.5)**





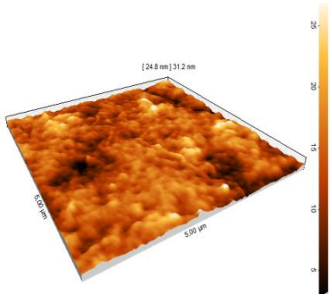




3D(1/0)

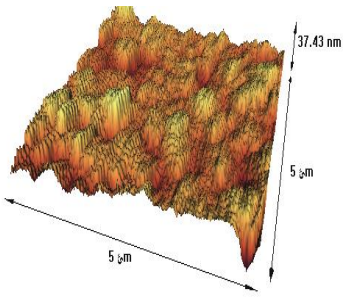
3D(1/0.25)

3D(1/0.5)

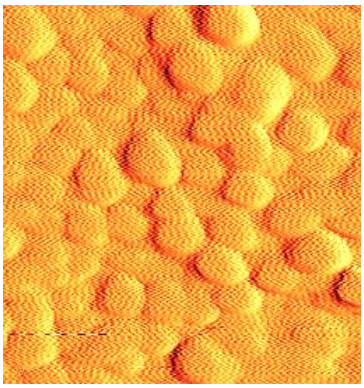


3D(1/0.75)

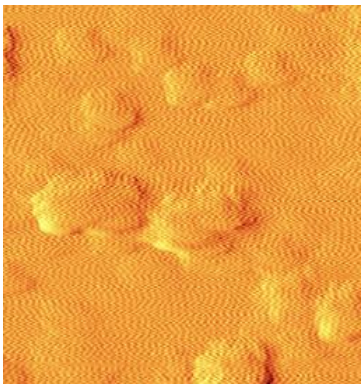
(a) As-deposited films



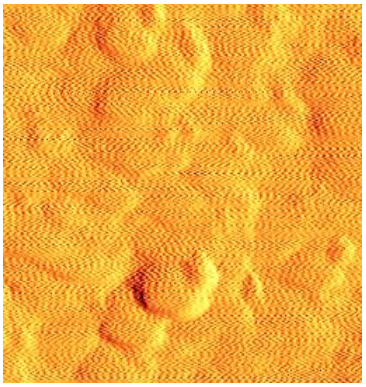
3D(1/1)



2D(1/0)a



2D(1/0.25)a



2D(1/0.5)a

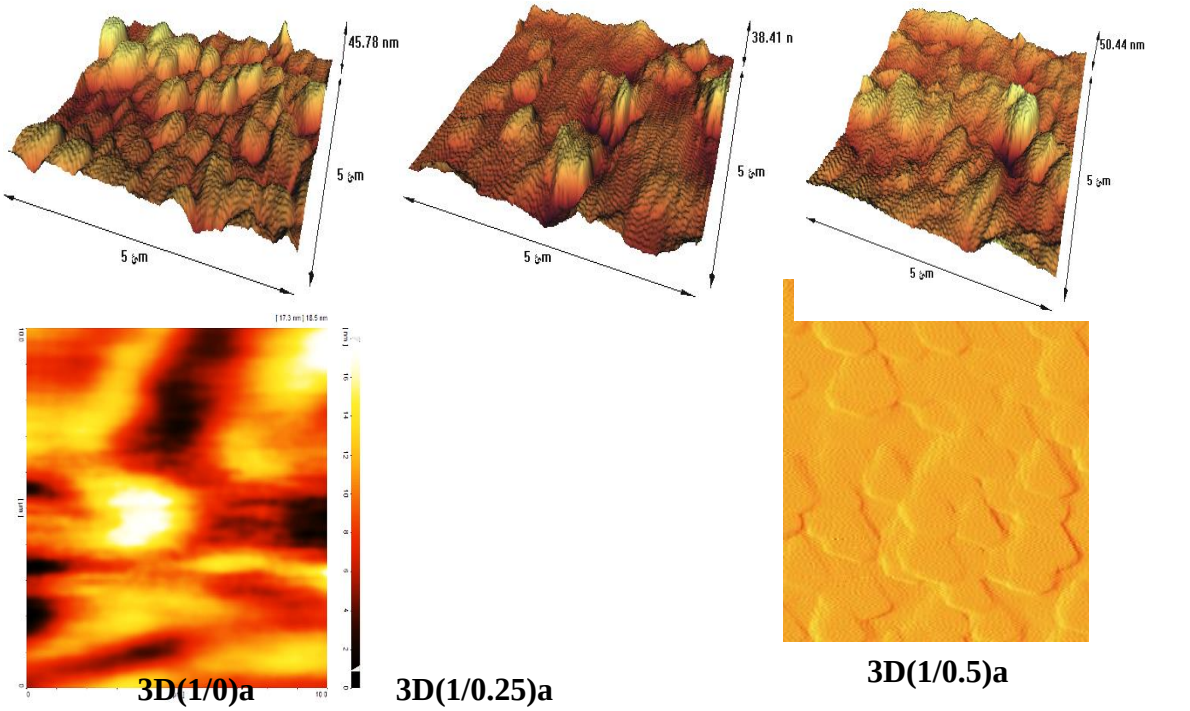


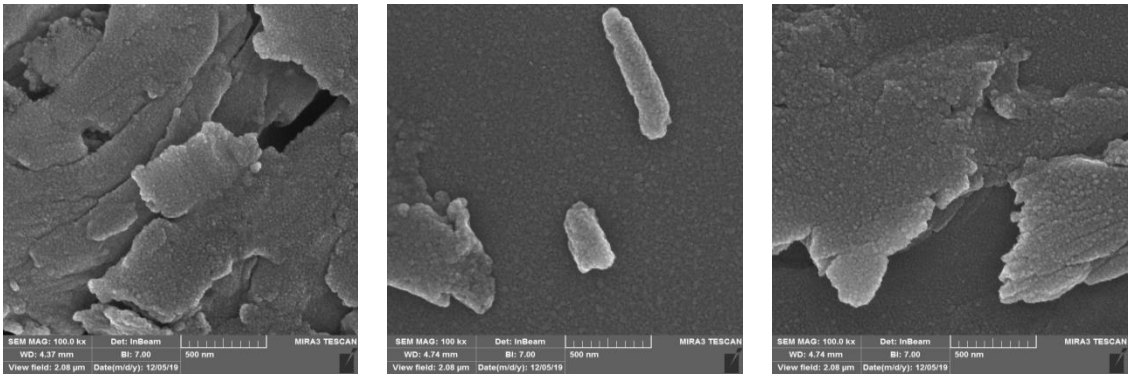
Figure 3-2-D and 3-D AFM images of GO/ PEDOT:PSS thin films.

Table 1-Average diameter and rout mean square roughness for as-deposited and annealed GO/ PEDOT:PSS thin films.

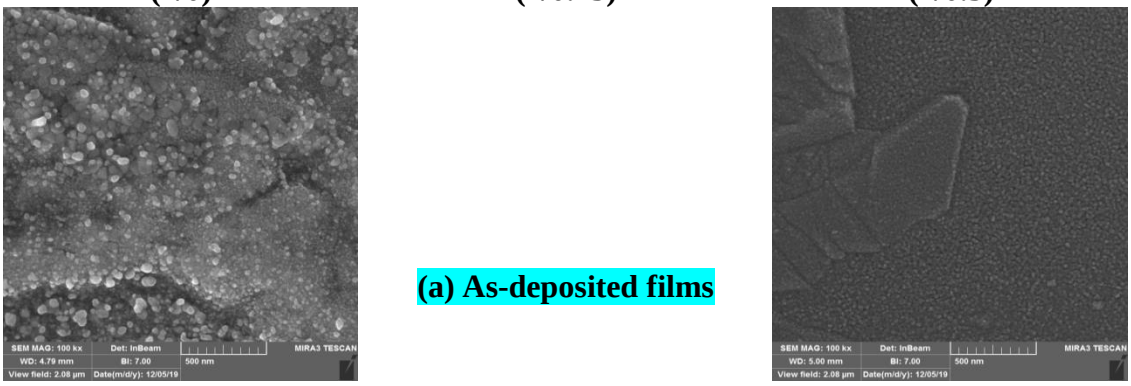
Sample	As-deposited		Annealed	
	D_{avg}(µm)	$R_{r.m.s}$(nm)	D_{avg}(µm)	$R_{r.m.s}$(nm)
1/0	0.510	12.34	0.569	10.90
1/0.25	0.745	6.484	0.784	2.832
1/0.5	0.686	5.075	0.765	5.034
1/0.75	0.59	14.3	1.1	3.34
1/1	0.725	9.241	0.647	7.397

The surface morphologies of the as-deposited and annealed GO/ PEDOT:PSS thin films using FESEM shown in Figure 4 GO thin film turns out to be porous due to its wrinkle shape which indicate a high surface area to volume ratio [14]. The polymer adding of PEDOT:PSS also

change the morphology of the GO sheets. One can see from Figure 4(a), A small amount of PEDOT: PSS loads itself to the GO flakes uniformly and makes the paper surface smoother than the original GO surface as shown in AFM images, by increasing the concentration of PEDOT:PSS, PEDOT:PSS clumping may occur from aqueous dispersion, appear as spherical granules on GO flakes and filament-shaped (1/1) [12].The good embedded of PEDOT:PSS on GO sheets belong to the interaction of GO and PEDOT:PSS vio two ways, the first is the π-π interaction of π bonds in GO with PEDOT chains which have plenty of π bonds, the second one is the hydrophilic-hydrophilic interaction between these to materials due to hydrophilic groups excist in GO and PSS chains [15]. The same actions occur on the films after annealing process as appear in Figure 4(b) but with degreasing in both GO sheet length and grain size of PEDOT:PSS.

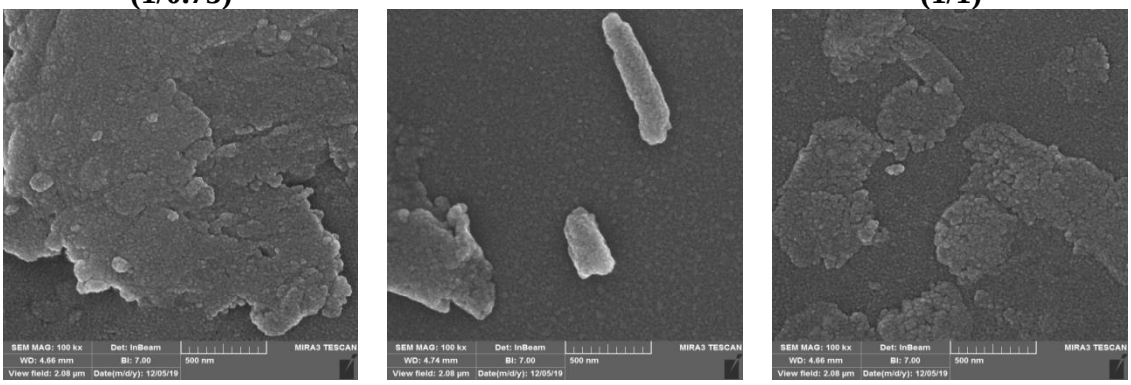


(1/0) **(1/0.25)** **(1/0.5)**

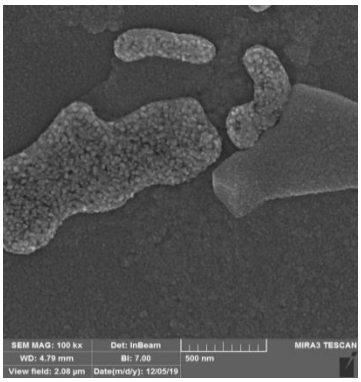


(1/0.75) **(1/1)**

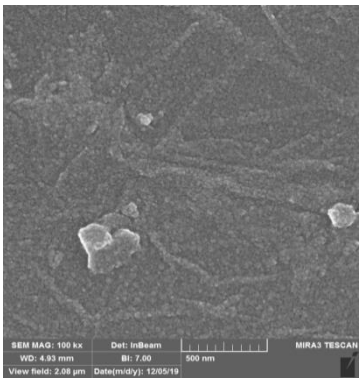
(a) As-deposited films



(1/0)a **(1/0.25)a** **(1/0.5)a**



(b) Annealed films



(1/0.75)a **(1/1)a**

Figuer 4-Field emission scanning electron microscopy images of GO/ PEDOT:PSS thin films.

Conclusion

The GO/PEDOT:PSS nanocomposite thin film was successfully prepared using spin coating technique. The good dispertion and distribution of PEDOT:PSS in GO was clearly observed via AFM and FESEM images and supported by XRD patterns which confirm the immobilized of PEDOT:PSS on GO sheets by take the former the orientation of GO in all prepared films. The increase of PEDOT:PSS concentration lead to agglomeration and may be separate it form GO sheets. The benefit of these properties lies in the sensors and solar cells.

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