Effect of annealing and chemical treatment on structural and optical properties of CuPcTs/PEDOT:PSS (BHJ Blend) thin films

Mahdi H. Suhail and Amer A. Ramadhan
Department of Physics, College of Science, University of Baghdad
E-mail: amer23_2005@yahoo.com

Abstract

In this work, The effect of annealing treatment at different temperatures (373, 423 and 473) K and chemical treatment with talwen at different immersion time (40, 60 and 80) min on structural and optical properties of the bulk heterojunction (BHJ) blend copper phthalocyanine tetrasulfonic acid tetrasodium salt/poly dioxyethylenethienylene doped with polystyrenesulphonic acid (CuPcTs/PEDOT:PSS) thin films were investigated. The films were fabricated using spin coating technique. X-ray diffraction (XRD) measurements displayed only one peak at $2\theta = 4.5^o$ corresponding to (001) direction which has d_{hkl} larger than for standard CuPcTs. The d_{hkl} increase then decrease with increasing annealing temperature and the time of chemical treatment with talwen. FTIR measurements show that, the peaks for O-H, in general, decrease with increasing annealing temperature, while the peaks corresponding to C=C aromatic bond and C-N bond decrease at 373 K then increase at 423 and 473 K. The peaks for O-H, in general, decrease with increasing immersing time, while the peaks corresponding to C=C aromatic bond and C-N bond decrease at 40 min then increase at more immersing time. From UV-visible measurements, the absorption spectra peaks for B and Q-bands increase at 373K and at 40 min immersing time with talwen and decrease at more annealing or chemical treated time.

Key words
CuPcTs/PEDOT:PSS, optical properties, X-ray diffraction.

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تأثير التلدين و المعاملة الكيميائية على الخصائص التركيبية والبصرية للاغشية الرقيقة CuPcTs/PEDOT:PSS

مهدي حسن سهيل و عامر عباس رمضان
قسم الفيزياء، كلية العلوم، جامعة بغداد

الخلاصة

تم في هذا البحث دراسة تأثير التلدين ولدرجات حرارة مختلفة (373 و 423 و473) كلفن و المعاملة الكيميائية باستخدام مادة التلوين وبأزمان غمر مختلف (40 و60 و80) دقيقة على الخصائص التركيبية والبصرية لغشاء مزيج ملح نحاس– فثالوسيانين الرباعي ملح الصوديوم مع مادة حامض كبريتات البوليستيرين (CuPcTs/PEDOT:PSS) المحضر بطريقة الطلاء الدوراني. ظهر في دراسة حيود الاشعة السينية قمة واحدة بحدود 4.5 درجة والتي تخص الاتجاه (001) والتي تمتلك قيم اصغر للمسافة البينية للمستويات البلورية (d_{hkl}) مما في قيم CuPcTs القياسية. قيم ال d_{hkl} تزداد ثم تقل مع زيادة درجة الحرارة و تقل مع زيادة زمن المعاملة الكيميائية مع التلوين. بينت قياسات مطياف تحويل فورير للأشعة تحت الحمراء أن القمم التي تخص O-H بصورة عامة تقل شدتها بزيادة درجة حرارة التلدين. بينما القمم التي تخص كل من الاواصر C=C الاروماتية و الاواصر C-N تقل عند 373 كلفن ومن ثم تزداد عند 423 و473 كلفن. القمم التي تخص O-H بصورة عامة تقل شدتها بزيادة زمن العاملة الكيميائية. بينما القمم التي تخص كل من الاواصر C=C الاروماتية و الاواصر C-N تقل عند 40 دقيقة ثم تزداد لزمن معاملة اكثر مع التلوين. من قياسات طيف الامتصاص للأشعة فوق البنفسجية- مرئية، أن قمم امتصاص الحزمة B و Q تزداد عند درجة حرارة تلدين 373 كلفن وعند 40 دقيقة زمن غمر بمادة التلوين ثم تنخفض عند تلدين او زمن معاملة أكثر.

Introduction

Over the last two decades, organic semiconductors have more attention because of using in many applications such as gas sensors [1], solar cell [2] and detectors [3], because there chemical variety which can able to change their properties [4].

Phthalocyanine has thermal and chemical stability due to its chemical composition. Adding four sulfonate groups SO^{-3} to the Pc ring for CuPc make him soluble in water to use it in many applications. CuPcTs (Its molecular formula is ($C_{32}H_{12}CuN_8O_{12}S_4Na_4$) has 984.25 g/mol molecular weight) has two absorption peaks, Q - peak near 660 nm and B- peak at about 350 nm [5]. PEDOT was initially found to be an insoluble polymer. The solubility problem was then avoided by using a water-soluble polyelectrolyte, poly (styrene sulfonic acid) (PSS), as the charge-balancing dopant during polymerization to yield PEDOT: PSS. This combination yields a water-soluble polyelectrolyte with a good film forming properties, high conductivity, transmission to visible light, and stability [6].

The most efficient organic photovoltaic based on bulk heterojunctions using two organic semiconductors in blend, by mixed them in solution then fabrication thin films to get large donor-acceptor interface area[7]. The properties of organic semiconductor especially phthalocyanine family can be enhance either by thermal [8, 9] or chemical treatment [10, 11]. Low temperature heat treatment was required in organic thin films for modification by reducing the surface native oxide or by enhancing the crystallization. The PEDOT:PSS films are stable under heat treatment and decomposition occurs above 663 K [8].

Various methods for the removal of endodontic fillings via suitable solvents retreatment have been proposed, by immersing in the selected solvents. The selection of an ideal solvent requires a balance between surface modification of MPcTs and effectiveness in chemical dissolving [12]. Structural and optical properties modification of the active layer by immersing with low solubility solvents of talwin (via increment in light absorption or charge transport) improve the device performance [13].

The effect of annealing treatment, at different temperatures, and chemical treatment with talwen at different immersion time were investigated.

Experimental

CuPcTs from Sigma-Aldrich company was fully dissolved in de-ionized water (15 mg/ml) by magnetic stirrer in about 12 hour, on two periods, at 310 K. The solution was filtered using (0.45) µm filter to remove any undissolved material. The prepared CuPcTs solutions were mix with PEDOT:PSS (1:1) wt% to make CuPcTs/PEDOT:PSS by magnetic stirrer in about 12 hour at 310 K. The solution was filtered using (0.45) µm filter.

Glass substrates of size 2.5×2.5 cm^2 were cleaned by soaking them sequentially with a detergent solution and rinsed them by water. Three stage of cleaning using ultrasonic for 20 min for each one, using water, alcohol and acetone, and then dried by blowing air and wiped soft papers.

The blend was deposited on the glass substrate by spin coating technique with 1500 rev/min speed for 2 minute time in air at room temperature to make organic thin films. The films were annealed at three temperatures (373, 423 and 473) K, and other samples treated with organic solvent (Talwen) at different treated time (40, 60 and 80) min to study the optimum conditions, annealing temperature and treated time with talwen, to improve the blend films properties.

All films were examined by X ray diffraction (type Shimadzu) to study its structural properties, FTIR (from Shimadzu company) to study the effect of annealing and chemical treatment on chemical bonds, and UV-visible spectrophotometer (supplied by Shimadzu company) in the wavelength range (300 to 1100) nm to study films absorbance and energy gaps variations with annealing and chemical treatments.

X-ray diffraction Bragg's law was used to calculate inter-planar distance d_{hkl} from the condition of constrictive interference of X-ray diffracted from parallel planes atoms [14].

$$n\,\lambda = 2\,d_{hkl}\sin\Theta \qquad (1)$$

where λ, Θ and n represent X-ray wavelength from Cu target (1.5406 Å), diffraction angle and diffraction order respectively.

The X-ray diffraction peaks full width at half maximum (FWHM) used to determine the crystalline size as shown in Scherrer formula [15].

$$\mathrm{G.S} = \frac{0.9\,\lambda}{\mathrm{FWHM}\,.\cos(\theta)} \qquad (2)$$

while the absorption coefficient (α) which is defined as the relative number of the photons absorbed per unit distance of a semiconductor was calculated according to beer-lambert equation [16].

$$I = I_o e^{-\alpha t} \qquad (3)$$

where I_o and I are the incident and the transmitted photon intensity respectively and t is the thickness of the material. The equation can be rewritten as:

$$\alpha = -\frac{\ln(T)}{t} = 2.303\,\frac{A}{t} \qquad (4)$$

The electron transitions between the V.B. and the C.B. obey to Tauc equation [17]

$$\alpha h\upsilon = B\,(h\upsilon - Eg)^r \qquad (5)$$

where B is a constant inversely proportional to amorphousity, r=1/2, 3/2, 2, 3 for allowed direct, forbidden direct, allowed indirect, forbidden indirect transitions respectively.

Results and discussions

Fig. 1 shows the X-ray diffraction (XRD) patterns for as deposited CuPcTs/PEDOT:PSS blend thin films on glass substrate and thermal treated with different annealing temperatures. This figure shows that all films have one peak at about $2\theta = 4.5^0$ which has 2θ shift toward less values from standard CuPcTs peak in the direction (001), i.e. increasing in d_{hkl} values as a result of mixing PEDOT:PSS with CuPcTs. The intensity of the peak increase with increasing annealing temperature to 373K then decrease at 423 annealing temperature. The material convert to amorphous structure at 473 K. It shows that within a low annealing temperature improves the structural properties of the thin film. It is well established that crystalline and amorphous phases in variable amount co-exist in most of the organic semiconductor materials around glass transition temperature (T_g) of MPcTs [18]. While increasing annealing leads to worsen the crystallinety. The extended band located at around 24° is due to the glass substrate [19]

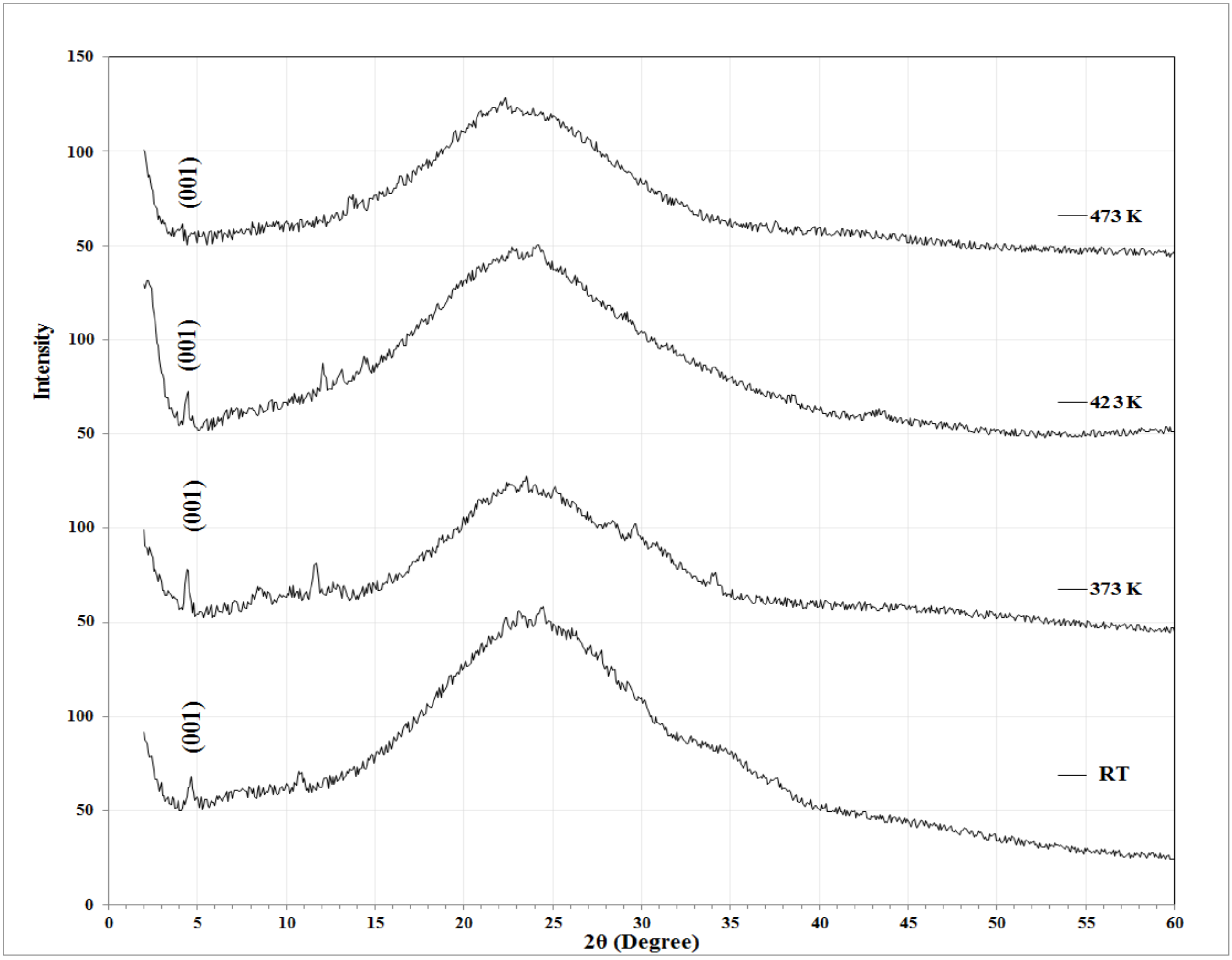

Fig. 1: XRD patterns for CuPcTs/PEDOT:PSS thin films deposited on glass substrate annealed at different temperatures.

Table 1 illustrates the comparison between experimental inter molecular plane distance (d_{hkl}) for CuPcTs/PEDOT:PSS blend thin films deposited on glass substrate annealed at different temperatures, calculated using Bragg law, and standard d_{hkl} value for CuPcTs [18, 19]. Crystalline size (G.S), calculated using Sherrer's formula. The G.S decrease at 373K then increase at 423 K annealing temperature.

Table 1: Structural parameters for CuPcTs/PEDOT:PSS thin films deposited on glass substrate annealed at different temperature.

T_a (K)	2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.(Å)	FWHM (Deg.)	G.S (nm)	hkl	phase
As deposited	4.635	19.0500	12.640	0.354	22.5	(001)	CuPcTs
373	4.450	19.8409	12.640	0.420	18.9	(001)	CuPcTs
423	4.455	19.8187	12.640	0.310	25.7	(001)	CuPcTs
473	Amorphous						

Fig. 2 illustrates the XRD patterns for as deposited CuPcTs/PEDOT:PSS blend thin films on glass substrate and chemically treated with talwen at different immersing time (40, 60 and 80 min). This figure shows that as deposited film and chemically treated at 40 and 60 minute have one peak at about $2\theta \approx 4.5^{o}$ which has shifted toward lower values comparing with the standard CuPcTs peak in the direction (001), i.e. increasing in d_{hkl} values as a result of mixing PEDOT:PSS with CuPcTs. Intensity decrease with increasing immersing time from 0 to 60 min then decreased at 80 min.

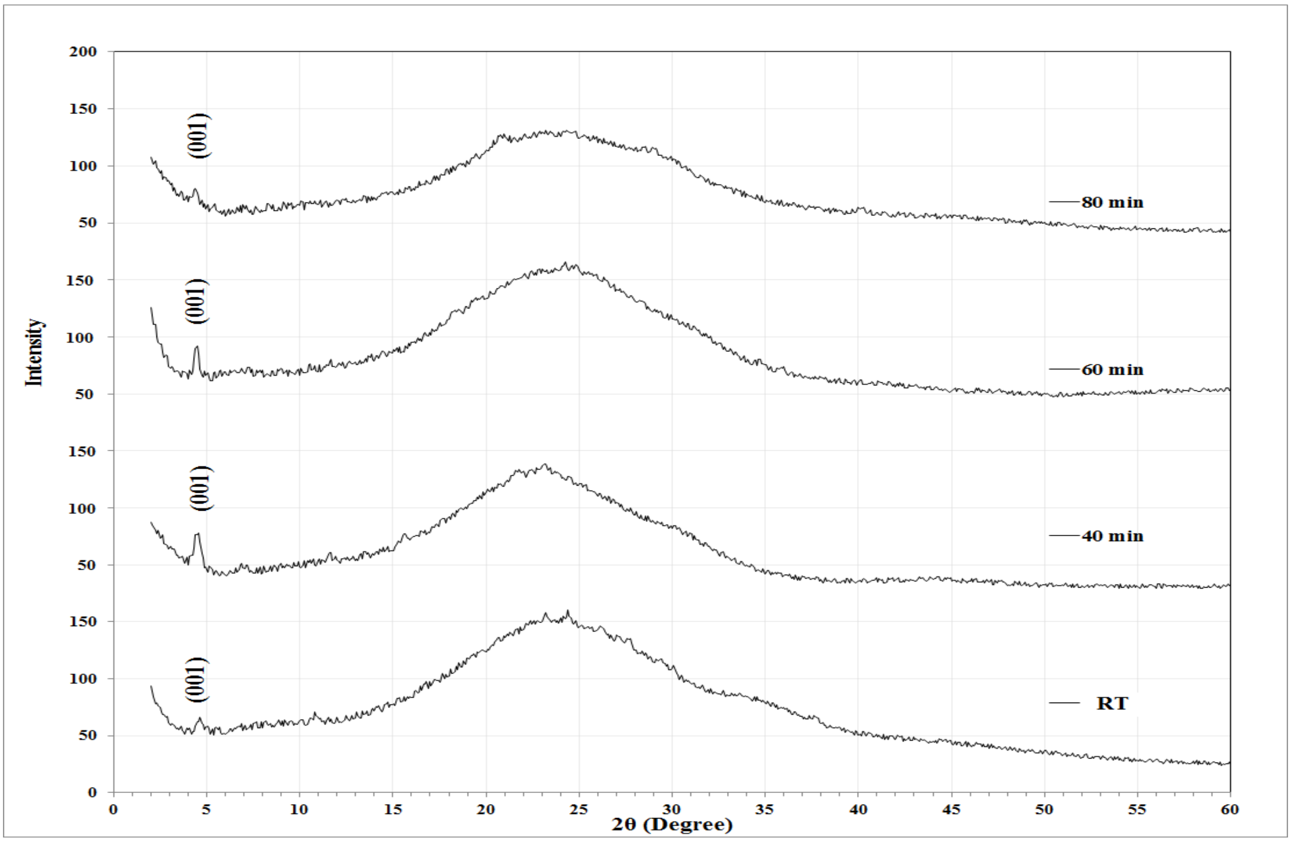

Fig. 2: XRD patterns for CuPcTs/PEDOT:PSS thin films deposited on glass substrate chemically treated with talwen at different time.

Table 2 illustrates the comparison between experimental (d_{hkl}) for as deposited at room temperature (RT) CuPcTs/PEDOT:PSS blend thin films on glass substrate and chemically treated with talwen at different immersing time and standard value for CuPcTs and crystalline size (G.S). The (G.S) decrease at 40 min then increase at 60 and 80 min immersing time.

Table 2: Structural parameters of CuPcTs/PEDOT:PSS thin films chemically treated with Talwen at different immersing time.

time (min)	2θ (Deg.)	d_{hkl} Exp.(Å)	dhkl Std.(Å)	FWHM (Deg.)	G.S (nm)	hkl	phase
As deposited	4.635	19.0500	12.640	0.354	22.5	(001)	CuPcTs
40	4.479	19.7140	12.640	0.365	21.8	(001)	CuPcTs
60	4.457	19.8119	12.640	0.328	24.3	(001)	CuPcTs
80	4.304	20.5156	12.640	0.304	26.1	(001)	CuPcTs

Fig. 3 shows the FTIR patterns for as deposited and annealed CuPcTs/PEDO: PSS blend thin films at different temperatures (373, 423 and 473 K).

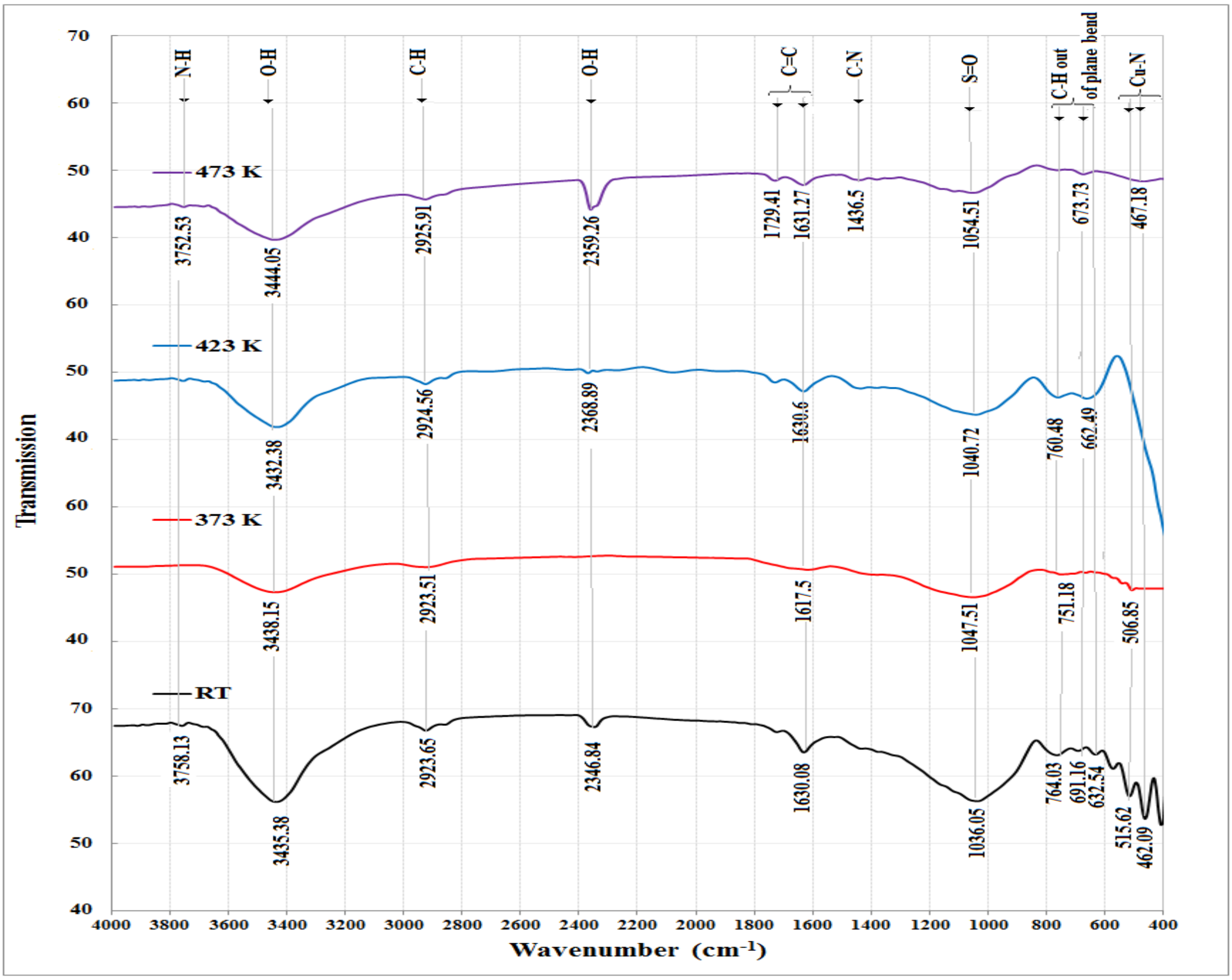

Fig. 3: FTIR patterns for CuPcTs/BEDOT:PSS thin films at different annealing temperatures.

In this figure the peaks locations were identified and match with the standard values [21]. The peaks, for RT sample, appear at (3758 for N-H bond, 3435 and 2346 for O-H bond, 2923 for C-H bond, 1630 for C=C aromatic bond, 1436 for C-N bond, 1036 for S=O bond 764, 691 and 632 C-H out of plane bend vibration, 515, 462 for Cu-N bond). We note that the peaks for O-H, in general, decrease in intensity with increasing annealing temperature. While the peaks corresponding to C=C aromatic bond and C-N bond decrease with 373 K then increase at 423 and 473 K.

The most of the peaks experienced a slight increase in energy bonds with annealing temperature 373 K which demonstrates the increasing atoms packing with annealing. Increasing annealing temperature up to 423 and 473 K leads to decrease energy bonds, as shown in Table 3 as a result of increasing atoms spacing with more annealing. These results are in agreement with X-ray results.

Table 3: FTIR bond for CuPcTs:BEDOT PSS thin films at different annealing temperatures

Ta (K)	N-H	O-H	C-H	C=C	C-N	S=O	C-H out of plane bend	Cu-N
As deposited	3758.13	3435.38 2346.84	2923.65	1630.08	-	1036.05	764.03 691.16 632.54	515.62 462.09
373	-	3438.15	2923.51	1617.5	-	1047.51	751.18	506.85
423	-	3432.37 2368.89	2924.56	1630.6	-	1040.72	760.48 662.49	-
473	3752.53	3444.04 2359.26	2925.91	1729.41 1631.27	1436.5	1054.51	673.73	467.18

Fig. 4 shows the FTIR patterns for as deposited CuPcTs/PEDOT:PSS blend thin films on glass substrate and chemically treated with talwen at different immersing time (40, 60 and 80 min).

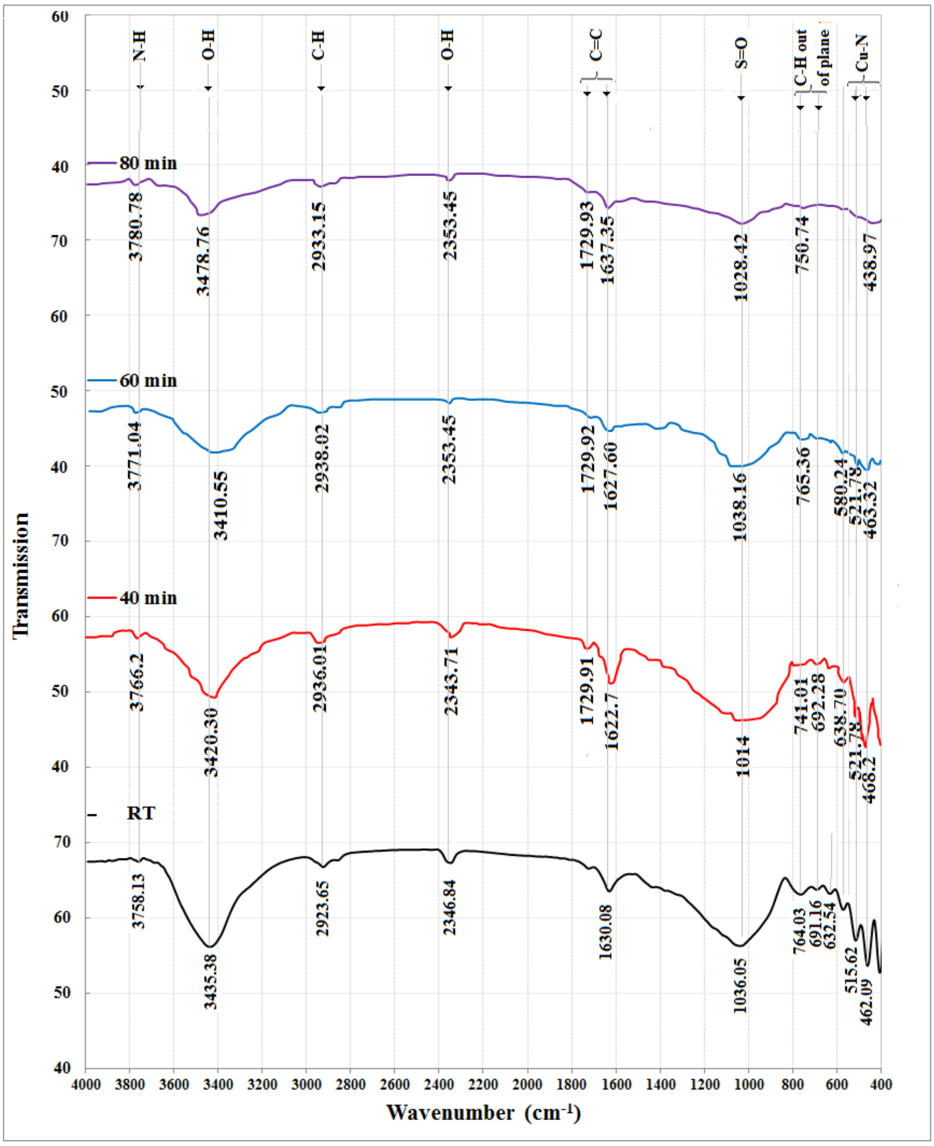

Fig. 4: FTIR patterns for CuPcTs:BEDOT PSS thin films chemically treated with talwen at different time.

In this figure peaks locations were identified and matched with standard values [22]. The peaks appear at 3758 for N-H bond, 3435 and 2346 for O-H bond, 2923 for C-H bond, 1630 for C=C aromatic bond, 1036 for S=O bond 764, 691 and 632 C-H out of plane bend vibration 515, 462 for Cu-N bond. Its observed that the peaks for O-H, in general, decrease with increasing immersing time. Also, it can be noted that C=C and N-H bonds experienced a slight decrease at 40 min then increase at more immersing time with talwen as shown in Table 4.

Table 4: FTIR bond for CuPcTs:BEDOT/PSS thin films chemically treated with talwen at different time.

Telwen	N-H	O-H	C-H	C=C	S=O	C-H out of plane bend	Cu-N
RT	3758.13	3435.38 2346.84	2923.65	1630.08	1036.05	764.03 691.16 632.54	462.09 515.62
40	3766.17	3420.30 2343.71	2936.01	1622.73 1729.91	1013.8	741.01 692.28 638.70	468.20 521.78
60	3771.04	3410.55 2353.45	2938.02	1627.6 1729.92	1038.16	765.36	463.32 521.78 580.24
80	3780.78	3478.76 2353.45	2933.15	1637.35 1729.93	1028.42	750.744	438.972

The peaks intensity corresponding to C=C aromatic bond increase and the peak corresponding to S=O being more broadening at 40 min which enhance the sample absorbance. Then the peaks intensities decrease at 60 and 80 min immersing time with talwen.

The absorbance for as deposited CuPcTs/BEDOT:PSS thin films and annealed at different temperatures (373, 423 and 473 K) deposited on glass substrate by spin coating are shown in Fig. 5. All samples have three peaks, one for B-band and two peaks for Q-band. The absorption peaks increase at 373 K annealing temperature, making the film to absorb more photons, i.e. produces more excited charge carriers. Making the sample more useful for use in many applications, such as photovoltaic devices [23]. The increment of absorption due to spectrum broadening so that absorbed light with wider range of wavelength. While more annealing temperature, at 423 and 473 K, the absorption become decreasing as a result of dissociation of some polymer molecules.

The Q band is due to the transition between the bonding and antibonding (π–π*) in phthalocyanine molecule. The central metal atom in MPcTs (copper) of the phthalocyanine molecule is associated with the d-band cause the strong absorption peak (B-band) attributed to π–d transitions[24]. These results are in agreement with Saipul et al. [25].

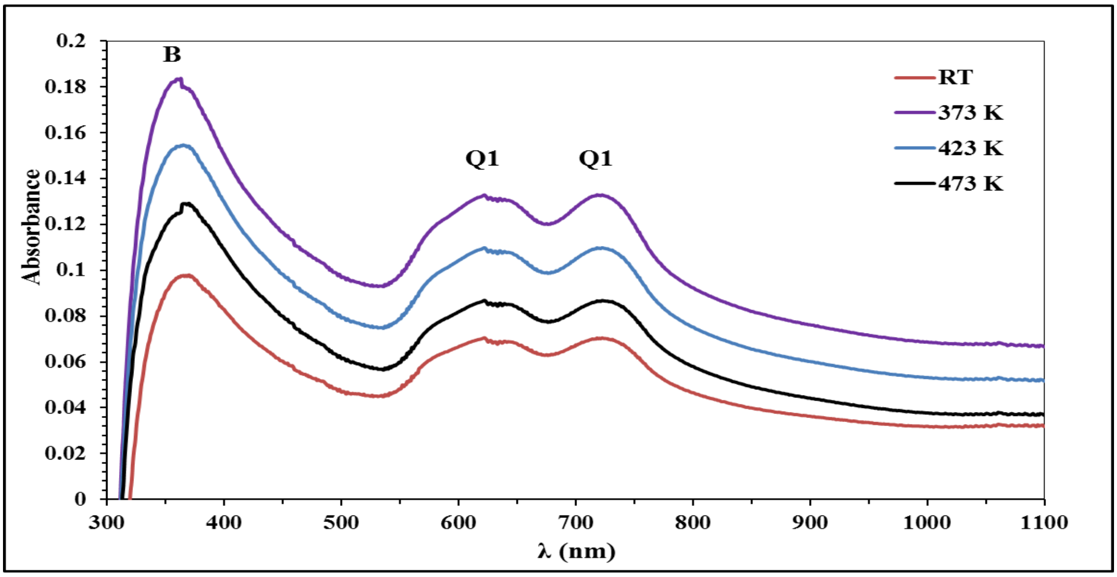

Fig. 5: Absorbance for the blend CuPcTs/PEDOT PSS thin films deposited on glass substrate annealed at different temperature.

Fig. 6 shows the variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of incident radiation for as deposited CuPcTs/PEDOT:PSS blend thin films and annealed samples at different temperatures.

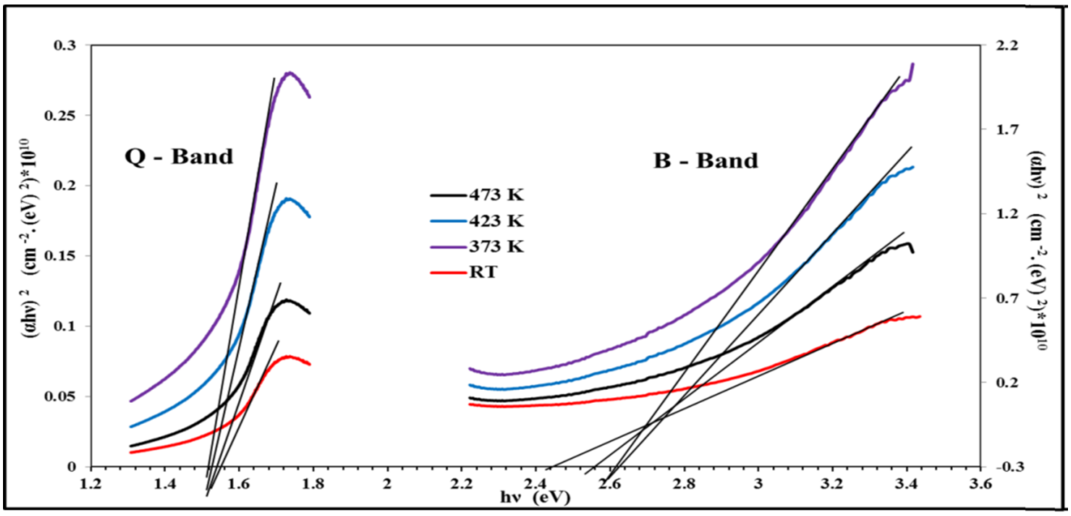

Fig. 6: $(\alpha h\nu)^2$ versus hν for the blend CuPcTs/PEDOT PSS thin films at different annealing temperatures for Q and B bands.

This figure shows that the value of optical energy gap for Q band decrease from (1.56 to 1.52) eV at 373K then increase to 1.54 eV when increasing annealing temperature to 473 K. While for B band increase from (2.44 to 2.62) eV up to 423K then decrease to 2.56 eV at 473 K annealing temperature, as shown in Table 5.

Table 5: Bands position and optical energy gaps of CuPcTs/PEDOT PSS thin films at different annealing temperatures.

Annealing temperature (K)	**B- band**	**Q-band**		**E_g (eV)**	
	peak position (nm)	**Q_1 peak position (nm)**	**Q_2 peak position (nm)**	**Q band**	**B band**
RT	357	614	716	1.56	2.44
373	357	617	717	1.52	2.60
423	361	627	717	1.53	2.62
473	363	617	720	1.54	2.56

The absorbance for as deposited CuPcTs/BEDOT:PSS thin films on glass substrate and chemically treated with talwen at different immersing time (40, 60 and 80 min) are shown in Fig. 7. There are one peak for B-band and two peaks for Q-band in all samples. The absorption peaks increase at 40 min immersing time with talwen. The increment of absorption because the enhancement of film structure. While increasing immersing time to 60 and 80 min cause decreasing in peak absorption as a result of allows the solvent molecules to be penetrate into the films and etching upper layer away. Peaks locations were included in Table 6. In general, there are small shift of the peaks location toward the short wavelength at 40 min and then reverse to become shifting toward the long wavelength when increasing immersing time to 60 and 80 min.

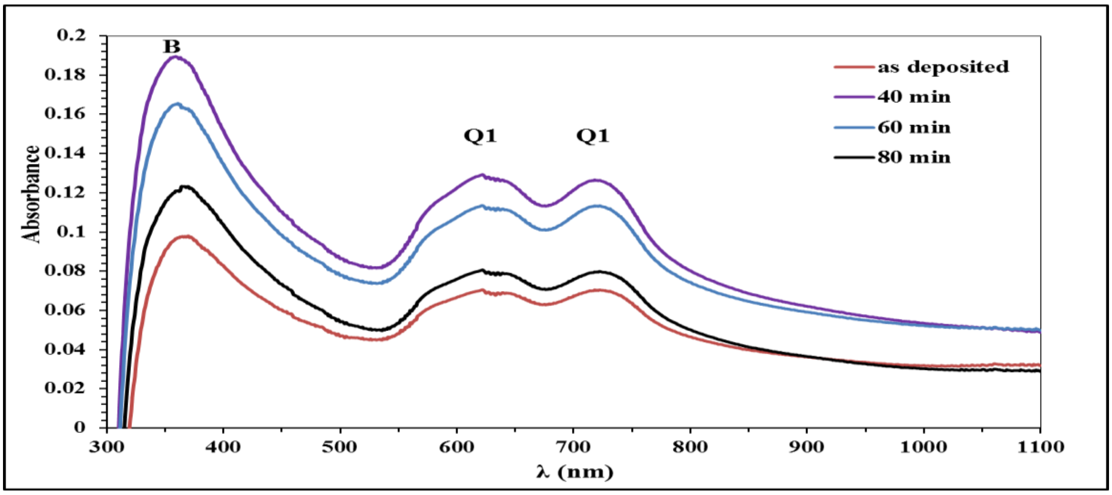

Fig. 7: The absorbance for the blend CuPcTs/PEDOT PSS thin films deposited on glass substrate chemically treated with talwen at different time.

Fig. 8 shows the variation of $(\alpha h\nu)^2$ versus photon energy (hν) of incident radiation for as deposited CuPcTs/PEDOT:PSS blend thin films chemically treated with talwen at different time.

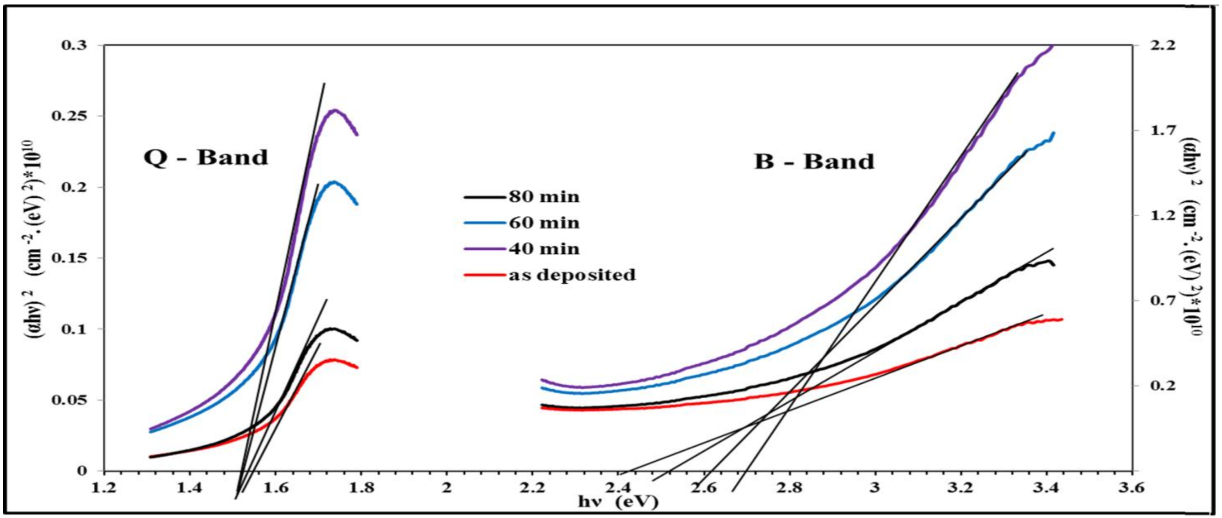

Fig. 8: (αhν)^2 versus hν for the blend CuPcTs/PEDOT:PSS thin films chemically treated with Chloroform at different time for Q band.

The value of optical energy gap for Q band decreases from (1.56 to 1.52) eV at 40 min immersing time then increase to 1.54 eV when increasing treatment time to 80 min. While for B band increase from (2.44 to 2.70) eV at 40 min then decrease to 2.52 eV at 80 min immersing time, as shown in Table 6.

Table 6: Bands position and the optical energy gaps of CuPcTs/PEDOT:PSS thin films chemically treated with Chloroform with different time.

Immersing time (min)	**B- band**	**Q-band**		**E_g (eV)**	
	peak position (nm)	**Q1 peak position (nm)**	**Q2 peak position (nm)**	**Q band**	**B band**
RT	357	614	718	1.56	2.44
40	353	616	712	1.52	2.70
60	356	617	713	1.52	2.62
80	360	618	718	1.54	2.52

Conclusions

The effect of thermal and chemically treatment with talwen on structural and optical properties of CuPcTs/PEDOT:PSS blend films were investigated. XRD measurements show that the d_{hkl} values less than standard CuPcTs values for all samples. The best annealing temperature and treatment time to enhance the crystallinety at 373K and 60 min chemical treatment with talwen. FTIR measurements indicate that the peaks intensities corresponding to C=C aromatic bond increase and the peak corresponding to S=O being more broadening at 40 min then, i.e enhance CuPcTs absorbance, while more immersing time with talwen cause to reduce the peaks intensities. Absorption spectra show the best treatment time with talwen is 40 min and the beast annealing temperature is 373 K at the point where the absorption peaks for B-band and Q-band have maximum values. The locations for Q and B bands experience a small shift with annealing and chemical treatment with talwen.

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