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Characterization of Copper Phthalocyanine-Tetrasulfonic Acid Tetrasodium Salt /Graphene Oxide

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Abstract

In this paper, the pure graphene oxide and copper phthalocyanine-tetrasolfonic acid tetrasodium salt were used to prepare thin films by using the spin coating method. These chemical compounds have remarkable optical properties and are chemically used in the development of device sensors by increasing the mixing ratio. Three different mixing ratios were prepared at room temperature and 150^{o}C annealing temperature for three hours. The spectra of UV-VIS-IR absorption, photoluminescence, and Fourier-transformed infrared (FT-IR) were studied.

Keywords: Graphene oxide, Cupper phthalocyanine tetrasolfonic acid tetra sodium salt, Spectroscopic.

توصيف المتراكبات لأوكسيد الكرافين /فثالوسيانيين نحاس رباعي حامض الكبريتيك رباعي املاح الصوديوم النانوية

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الخلاصة

تم استخدام أكسيد الجرافين النقي / فثالوسيانين نحاس رباعي حامض الكبريتيك رباعي املاح الصوديوم النانويه لإعداد الأفلام الرقيقة عن طريق طريقة طلاء تدور. هذه المركبات الكيميائية لها خصائص بصرية ملحوظة وتستخدم كيميائيا في تطوير أجهزة الاستشعار عن طريق زيادة نسبة الخلط. تم إعداد ثلاث نسب خلط مختلفة في درجة حرارة الغرفة ودرجة حرارة 150 لمدة ثلاث ساعات. وقد تمت دراسة امتصاص الأشعة فوق البنفسجية والأشعة الضوئية وأطياف الأشعة تحت الحمراء ذات التحولات السريعة.

Introduction

Graphene oxide (GO) is the oxidized form of graphene [1]. It is a single atomic layered material that is formed by the oxidation of graphite which is cheap and readily available. GO is easy to process since it is dispersible in water and other solvents [1]. Oxygen in its lattice graphene oxide form is not conductive, but it can be reduced to graphene by chemical methods. One of the main advantages of GO is that it is dispersible to water. This makes it possible to use in solution-based processes [2]. The primary method for fabrication of graphene films is the chemical vapor deposition (CVD) [3]. However, this method requires high temperatures and relatively long deposition times, making it expensive. It also limits the deposition to substrates that can tolerate high temperatures, making deposition on the top of polymers difficult .Solution-based methods include spray, spin, and dip

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coating as well as Langmuir-Blodgett (LB) deposition. Graphene has been subjected to an increasing attention in various areas of science and technology due to its remarkable physico-chemical properties [4]. Owing to the special two-dimensional structure, graphene possessed many unique properties that are different than those of carbon materials, including a high specific surface area (theoretically $2630m^2/g$ for single layer graphene)[5], extraordinary electronic properties and electron transport capabilities [6-8], and high thermal conductivity ($\approx 5000Wm^{-1}K^{-1}$) [9-10]. Thus, GO has important applications in areas related to transparent conductive films, composite materials, solar energy, and biomedical applications.

Copper- phthalocyanine (CuPc) has the chemical formula of C32H16N8Cu with one copper atom in the center of the ring and 16 hydrogen atoms surrounding the molecule. It is a planar molecule consisting of an inner porphyrin ring with four benzene rings located symmetrically at the four corners [11]. The structure of copper (II) phthalocyanine tetrasulfonic acid tetrasodium salt (Cu-PcTs) is very similar to that of CuPc, except that the polar SO3Na is joined to the benzene rings, which makes this complex water dissolvable [12]. The organic semiconductors have a great interest due to their usages in electrical, electronic, and photonic devices and sensors [13]. The purpose of this research is to study the effects of various mixing ratios of GO/Cu-PcTson on the spectra of UV-VIS-IR absorption, photoluminescence, and FT-IR.

Experimental design and methods

Colloid water-based nano graphene oxide with a concentration of 1 mg/ml was used in this work. Cu-PcTs powder was added to de-ionized water with a concentration of 10mg/1ml. Three different mixing ratios of GO were tested in this work, as shown in Table-1. Magnetic stirring for 60 minutes was used to mix and dissolve the two compounds at room temperature. Quartz was used as a substrate, being cut in a size of 2.5 x 2.5 cm and cleaned with acetone and distilled water after being placed in an ultrasound device. Finally, the quartz substrate was dried with a special drying paper. The different thin films were prepared using the spin coating method on quartz substrate with different spin coating speeds of 2000, 2000, and 300 rpm for 10s, 60s, and 10s, respectively. After studying the optical and spectroscopic properties, the thin films were annealed at 150^oC for three hours and their optical and spectroscopic properties were determined, as shown in Table-2. After the completion of the annealing of the thin films, a comparison was made between the two cases.

Results and discussion

The thickness of all samples was measured by using an optical interferometer method employing an He–Ne laser of 632.8nm wavelength λ, 1mW power, 1mm spot size, and Gaussian mode with an incident angle of 45^o. This method depends on the interference of the laser beam reflected from the thin film surface and the substrate; the films thickness (t) was determined using the following formula:

$$t = \frac{\lambda}{2}\frac{\Delta x}{x} \qquad (1)$$

where Δx is the distance between two adjacent fringes and x is the width of fringe. The thickness of the thin films prepared was 100 nm.

The UV-VIS-IR spectrum data, with a range of 190-1000 nm, of pure Cu-PcTs, pure GO, and samples of three different mixing ratios at RT are shown in Figure-1. The pure GO has four peaks at 219, 298, 419, and 622nm, with three peeks of pure Cu-PcTs at 219, 618, and 691nm. The spectrum of the three mixing ratios shows four peaks at 219, 291, 417, and 617 nm, with an increasing absorption intensity and red shift with decreasing the GO ratio, as shown in Table-3. In the 150^oC annealing temperature, as shown in Figure-2, the UV-VIS-IR spectra of the three mixing ratios tend to the pure Cu-PcTs spectrum. All peaks obtained from the absorption spectra of the samples are listed in Tables-3 and 4. It was found that there was a peak absorption of GO at 220nm due to the electronic transmission (π-π^*) resulting from the presence of double bonds (C=C) in GO or the remaining of the original graphite. It can also be observed that there is an absorption peak at 298nm related to the electronic transmission (n-π^*), which is due to the carbonyl group (C=O) in the GO. The annealed films at 150◦C show the highest absorption, whereas the lowest was at RT.

The $(\alpha h\upsilon)^2$ as a function of photon energy for all thin films is shown in Figure-3 and Figure-4 at RT and 150^oC annealing temperature, respectively. The variation of $(\alpha h\upsilon)^2$ was estimated by the Tauc's Equation[14]:

$$(\alpha h\upsilon) = A\,(h\upsilon - E_g)^n \qquad (2)$$

where *as* is the absorption coefficient, *A* is a constant, *hv* is the incident photon energy, and E_g is the optical energy band gap. This equation used n=1/2 for direct transition. The extrapolation of the linear part of the plot, $(ahv)^2=0$, gives rise to the estimation of the E_g value of all prepared thin films. Table-3 shows the E_g values of all prepared samples. It is observed that the E_g value is 4.2eV for the pure GO and 4.73eV for the pure Cu-PcTs. The effects of energy band gap disappeared at the mixing ratio of 1:1, but it increased with decreasing the GO ratio. Moreover, the energy gap results of the sample at 150°C annealing temperature are shown in Table-4, where the energy gap for the pure GO is 3.22eV, whereas it was 4.66 eV for the pure Cu-PcTs and the other mixtures. This reduction is attributed to the life of the localized states inside the gap due to the amorphous shape of CuPcTs/GO upon treatment with this temperature (150°C).

The photoluminescence spectra at 230 and 325nm excitation wavelength of all samples at RT and 150°C are shown in Figures-5, 6, 7 and 8, respectively. Tables-3 and 4 shows all the peaks obtained from the four figures. In these figures, note that the spectra of the three mixing ratios are near to the same peaks of the pure GO, but they are different in intensity. The intensity of PL spectrum decreases with the mixing process and reaches the lowest value at the lowest mixing ratio (1:0.5). Then it starts to increase with increasing the mixing ratio. One of the most interesting photoluminescent properties of graphene oxide is that the emission wavelength is determined by the degree of oxidation of grapheme [15]. The annealed films at 150°C show the highest emission intensity, whereas the lowest was at RT.

The FT-IR measurements of Go and Cu-PcTs were used to identify the type and function of the bonds in the range of wave length 400-4000Cm^{-1} . FTIR spectra of Cu-PcTs showed pecks at 3461, 1631, 1396, 1215, 948, and 487 cm^{1-}, while those of GO showed pecks at 3450, 1633, 1396, 1072, 634, and 491 cm^{1-}. However, at different mixing ratios, some new peaks appeared, especially at samples M21 and M31. The peaks in all samples after annealing were shifted in the smallest bond energy, with the appearance of new peaks with widening peaks width and increased height in the samples of CuPcTs (2923 , 2364 , 1635 , 1220 , 952 , 756 , and 493cm^{1-}) and GO (3463 , 1643 , 1218 ,9431 , 624 , 484 , and 424cm^{1-}). The bond energy data of all samples are shown in Tables-5 and 6.

The FTIR spectra of GO, Cu-PcTs, and the different mixing ratios of the thin films have normal vibration modes.. For some bonds (C-H bonds of benzene, N-H bond, C-C bond, C-N bond, C=C bond, and C=N bond), it can be observed that the length of the bonds increased after annealing. This outcome has an exact agreement with the results reported by Hussein [16].

Conclusions

From this work, we conclude that it is possible to obtain thin films in the nano-range size using the spray technique. The lower the ratio of GO, the higher the intensity of absorption, with a shift towards the long wavelength. This behavior is reversed at an annealing temperature of 150°C. Through photoluminescence spectra, we observed that the samples exhibited the behavior of the GO spectrum with increasing intensity. The FT-IR spectra of GO, Cu-PcTs, and the different mixing ratio thin films have normal vibration modes.

Table 1-Different mixing ratios at room temperature

Sample No.	Ratio of Cu-PcTs/GO
M11	PureCu-PcTs
M61	PureGO
M21	1:1
M31	1:0.75
M41	1:0.5

Table 2-Different mixing ratios at 150°C annealing temperature

Sample No.	Ratio of Cu-PcTs/GO
M12	PureCu-PcTs
M62	PureGO
M22	1:1
M32	1:0.75
M42	1:0.5

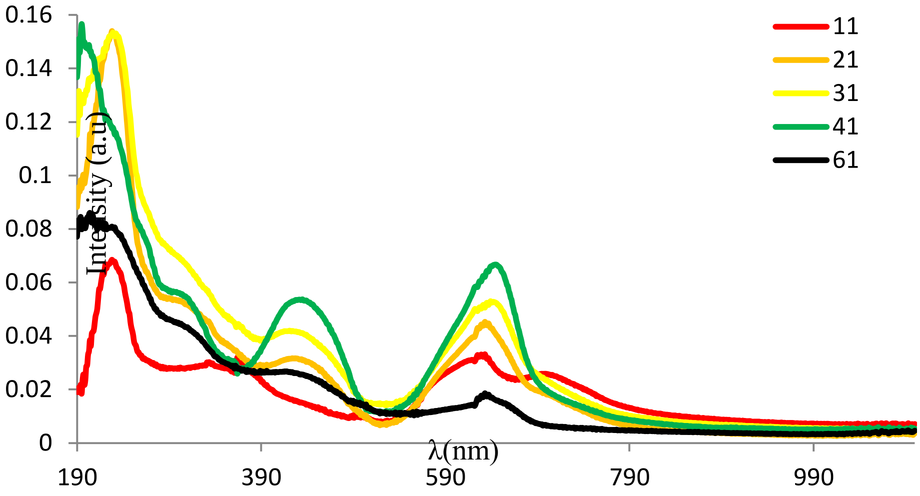

Figure 1-The UV-VIS-IR spectra of samples at RT.

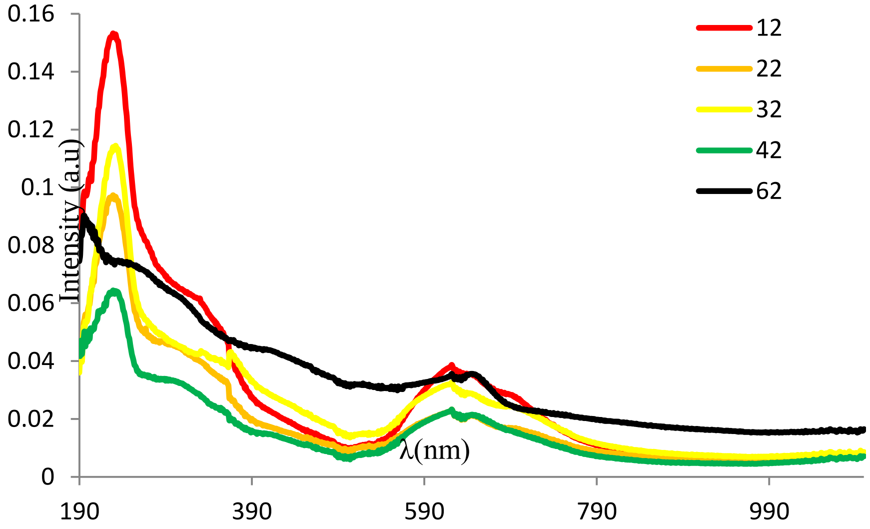

Figure 2-The UV-VIS-IR spectra of samples at 150°C.

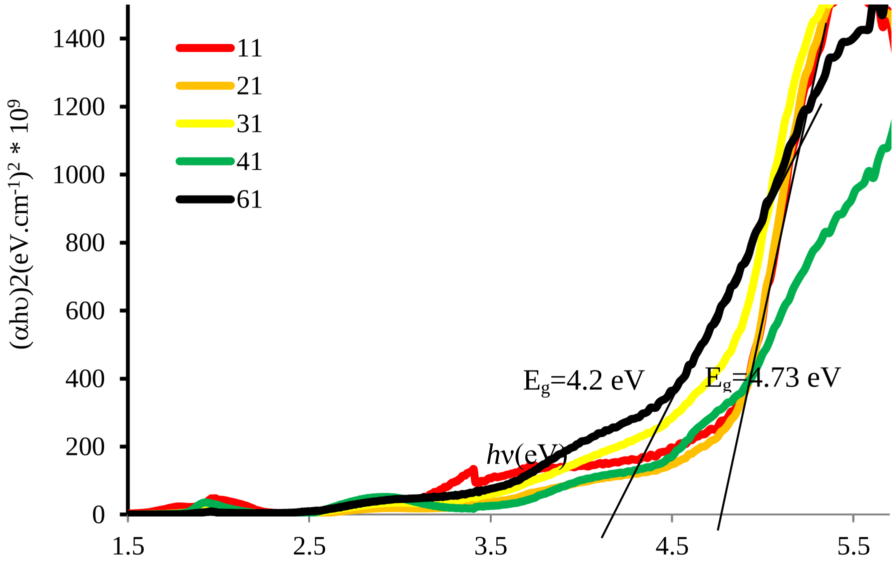

Figure 3- $(\alpha h\nu)^2$ Vs. photon energy($h\nu$) of samples at RT.

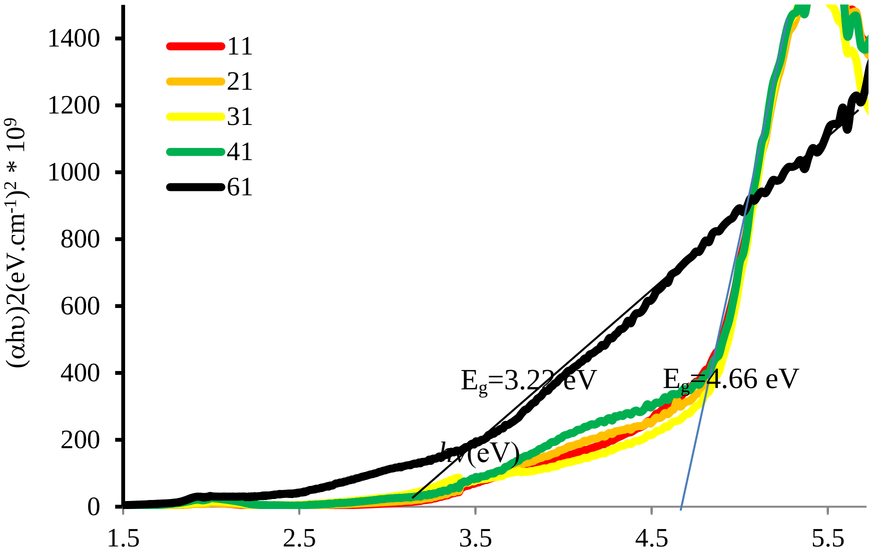

Figure 4- $(\alpha h\nu)^2$ Vs. photon energy($h\nu$) of samples at 150°C.

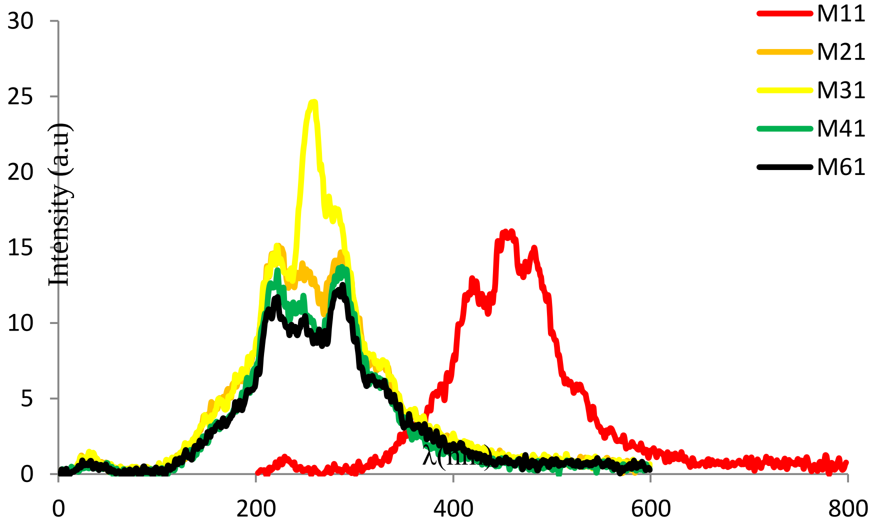

Figure 5- PL spectra of samples at λ_{ex} 230nm at RT.

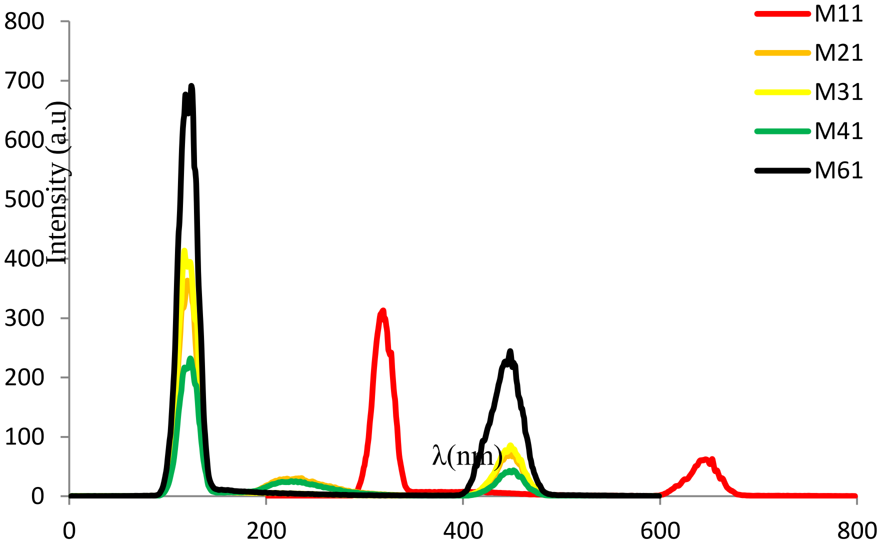

Figure 6- PL spectra of samples at λ_{ex} of 325nm at RT.

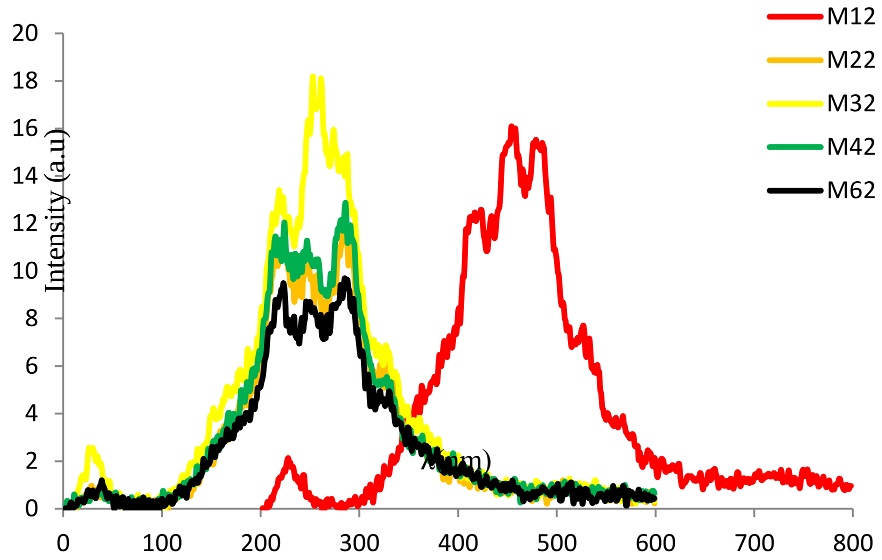

Figure 7- PL spectra of samples at λex of 230nm at 150 °C.

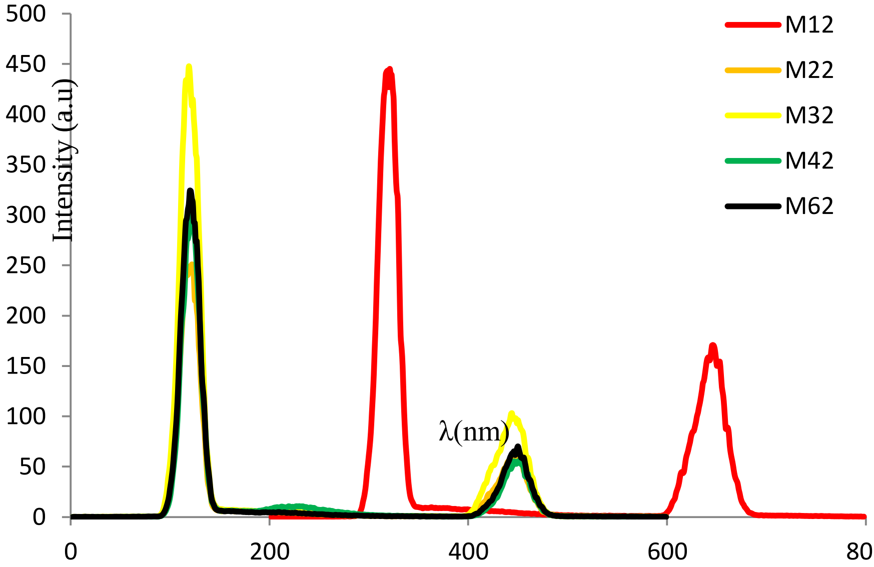

Figure 8-PL spectra of samples at λex 325nm at 150°C.

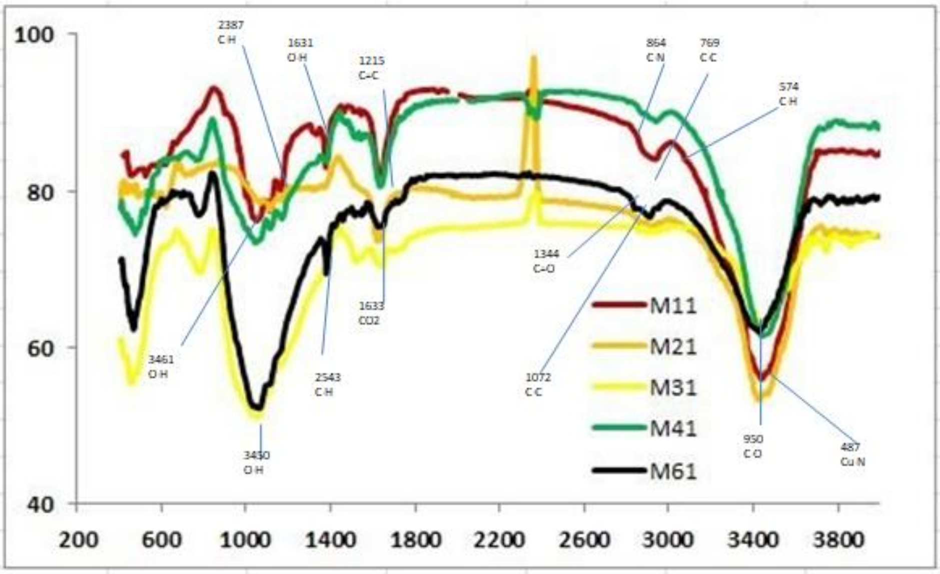

Figure 9-FTIR spectra of samples at RT.

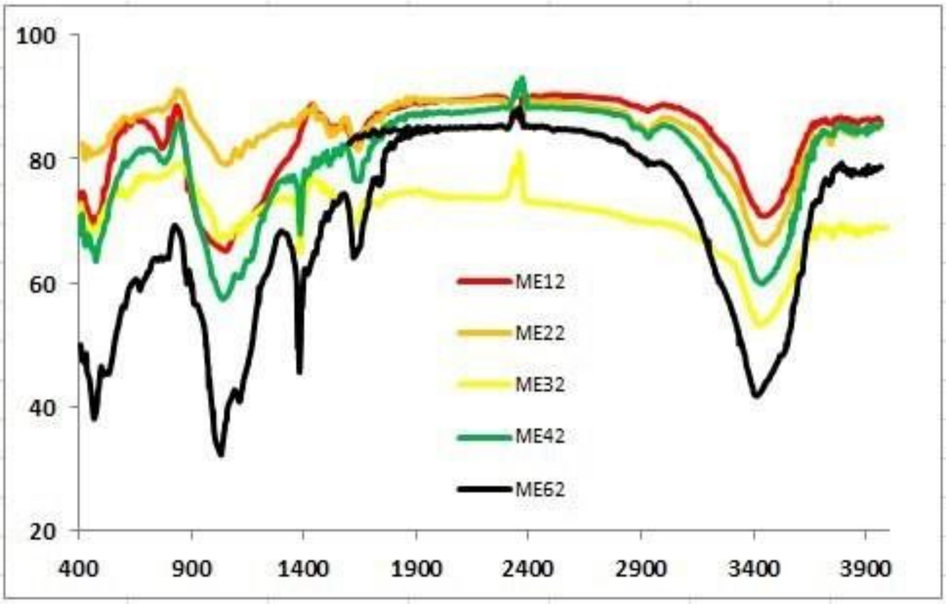

Figure 10- FTIR spectra of sample at 150 ^{o}C.

Table 3-The results of the most important parameters of samples at R

Sample No.	Maxing Ratio Cu-PcTs/GO	Absorption Peaks position(nm)	E_g(eV)	λexc 230nm	λexc 325nm
M11	Pure Cu-PcTs	219 618 691	4.73	230 415 445 473	315 634
M61	Pure GO	219 298 419 622	4.2	211 235 278	118 440
M21	1:1	219 291 417 617	4.2	211 235 278	109 435
M31	1:0.75	219 219 411 630	4.59	211 253 270	109 435
M41	1:0.5	192 219 419 631	4.5	211 235 278	109 435

Table 4-The results of the most important parameters of samples at 150^{o}C

Sample No.	Maxing Ratio Cu-PcTs/GO	Absorption Peaks position(nm)	E_g(eV)	λexc 230nm	λexc 325nm
M12	Pure Cu-PcTs	223 622 671	4.66	230 409 453 475	317 641
M62	Pure GO	246 631	3.22	215 246 281	119 440
M22	1:1	215	4.66	215	119

		614		246 281	440
M32	1:0.75	224 605	4.66	217 261	118 438
M42	1:0.5	219 605	4.66	215 246 281	119 440

Table 5-Bond energy values of CuPcTs.

Tem.	O-H	C-H	O-H	C-C	C-N	C-C	C-O	C-H	Cu-N
RT	3436	2358	1633	1182	964	773	698	615	487 460
150	3479 3456	2923	2364 2335	1635	862	765	696	640	493

Table 6-Bond energy of GO**.**

Tem	O-H	C-H	CO2	C=O	C-C	C-O
RT	3450 3438	2543	1633	1344	1072	950
150	3463 3440	2380	1643	1218	943	624

References

1. He, Klinowski, Forster, **1998**. "A new structural model for graphite oxide", *Chemical Physics Letters*, **287**(1): 53.
2. S.K. Tiwari, V. Kumar, A. Huczko, R. Oraon, A.D. Adhikari, G. Nayak Magic. **2016**. "al allotropes of carbon: prospects and applications", *Crit. Rev. Solid State Mater. Sci.*, **41**(4): 257.
3. Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V. **2009**. " Large Area, Few-layer graphene films on arbitrary substrates by chemical vapor deposition",*Nano Lett*, **9**(1): 30, 2009**.**
4. J. Zhao, L. Liu, and F. Li. **2015**. "Graphene Oxide: Physics and Applications", Springer.
5. M.D. Stoller, S. Park, Z. Yanwu, J.An, and R. S. Ruoff. **2008**. "Graphene-based ultracapacitors ",*Nano Letters*, **8**(10): 3498.
6. X. Li, G. Zhang, X. Bai. **2008**."Highly conducting graphenesheets and Langmuir-Blodgett films", *Nature Nanotechnology*, **3**(9): 538.
7. K.S. Novoselov, A.K. Geim, S.V. Morozov. **2005**. "Twodimensionalgas of massless dirac fermions in graphene",*Nature*, **438**(7065): 197.
8. K.S. Novoselov, Z. Jiang, Y. Zhang. **2007**. "Roomtemperaturequantum hall effect in graphene", *Sience*, **315**(5817): 1379.
9. A. A. Balandin, S. Ghosh, W. Bao et al. **2008**. "Superior thermal conductivity of single-layer graphene," *Nano Letters*, **8**(3): 902.
10. S. Ghosh, I. Calizo, D. Teweldebrhan, "Extremely highthermal conductivity of graphene: prospects for thermalmanagement applications in nanoelectronic circuits", *Applied Physics Letters*, **92**(15).
11. T.D. Anthopoulos, J.P.Markham, E.B. Namdas, J.R. Lawrence, I.D. Samuel, S.C. Lo and P.L. Burn. **2003**. "Influence of molecular structure on the properties of dendrimer light-emitting diodes", *Organic Electronics*, **471**.
12. PotjeKamloth, K. **2008**. "Semiconductor Junction Gas Sensors", *Chem. Rev.*, **108**: 367.
13. T. D. Anthopoulos, J. P. Markham, E. B. Namdas, I. D. Samuel, S. C. Lo and P. L. Burn, **2004**. "Solution Processable Red Phosphorescent Dendrimers for Light Emitting Device Applications"*Appl. Phys. Lett.*, **82**: 4824, 2004.
14. Tauc, J. **1974**. "*Amorphous and Liquid Semiconductors*", Springer.
15. Andrew T. Smith, Anna MarieLaChance, Songshan Zeng, **2019**. "Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites", *Nao material science*, **1**(1): 31.
16. M. T. Hussein, **2008**. "Theoretical IR spectroscopic study of Copper Phthalocyanine (CuPc)", **11**(2): 303.