Study of the properties of Multi-walled carbon nanotubes/ Carbon Quantum Dots Nanocomposites

Shaymaa A. AL- Kareem[1,*], Saeed .J. Abbas[2]

[1]*Department of Physics, College of Science, Al Basrah University.*

[2]*Department of Physics, College of Science, Al Basrah University.*

**Corresponding author E-mail : shymaa.shihab@uobasrah.edu.iq*

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Abstract: In recent years, there has been a growing interest in the synthesis and characterization of nanomaterials for various applications. Carbon nanotubes (CNTs) and quantum dots (QDs) are among the promising nanomaterials due to their unique properties. This study aims to synthesize and characterize multi-walled CNTs and QDs using the hydrothermal method. MWCNTs were synthesized at a temperature of 200°C using Ferrocene and Sulfur as precursors, while QDs were prepared at a temperature of 160°C using Polyethylene glycol (PEG). To fabricate the nanocomposite films, MWCNTs and QDs were mixed at different weight ratios (3:1, 2:2, and 1:3) through ultrasonic dispersion. The resulting mixture was then used to form films on glass surfaces. Characterization of the composites was carried out using a series of analyses including Fourier-transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and electrical conductivity measurements. From the FESEM measurements, spherical particles of various sizes were observed, with a wide size distribution of less than 10nm. XRD analysis revealed d-spacing values of 0.34nm, 0.39nm, and 0.46nm for all the mentioned weight ratios. Additionally, the diameter of the particles ranged from 32.48nm to 31.96nm, with a length of approximately 1μm. The electrical conductivity of the films was also measured, and the obtained results indicated activation energies of 0.155eV, 0.14eV, and 0.25eV for the respective weight ratios. The resulting nanocomposite films exhibited unique properties as characterized by various techniques. These findings contribute to the understanding and potential applications of nanomaterials in diverse

***Keywords*:** carbon quantum dots, hydrothermal method, Multi-walled carbon nanotube, Nanocomposite.

1. Introduction

Nanocomposites are materials with adding nanoparticles during the manufacture of these materials, and as a result, the nanomaterial shows a significant improvement in its properties. For example, adding carbon nanotubes changes the electrical and thermal conductivity properties of materials [1]. The addition of other types of nanoparticles may improve optical, dielectric, and mechanical properties such as hardness and strength. Because the ratio of surface area to volume of

nanoparticles is high [2]. The additions of small amounts of nanoparticles to polymers have enabled a newproperties for the composite materials. Still, results depend highly on the surface treatment of the nanoparticles and the processing used. It is crucial to determine whether nanomaterials could be integrated into nanocomposites to enable multiple desirable properties required for a given application [3].

Ajayan and colleagues [4]. Many papers in this area were published in the early 1990s, including many review articles focusing on various aspects of CNT nanocomposites [5-7], Chen et al. [8]. Discovered that adding graphene oxide (G.O.) to a PLA-PU (Polylactic Acid-Polyurethane) copolymer significantly improves the mechanical, thermal, and biological properties of the Composite when compared to PLA-PU alone. They also used the Composite to 3D print a cell scaffold and tested its cell viability. Additionally, Liu et al. [9] developed a surgical suture of a PLA composite reinforced with Multi-Walled Carbon Nanotubes (MWCNT) to increase mechanical resistance. They created a nanocomposite that increased bioabsorption time by up to 50% and strength correct time by 100%.

Carbon quantum dots (CQDs), fullerenes, carbon nanotubes (CNTs), graphene, and graphdiyne are all examples of carbon electronic materials[10].It has sparked a lot of interest since its discovery because of its intriguing properties, such as low toxicity, high chemical stability, environmental friendliness, ultracompact size, excellent photoluminescence, favorable biocompatibility, versatile surface, and superior electron transfer ability compared to other nanomaterials and organic sensors [11]. These are just a few of its characteristics.

CQDs have been utilized in electrophoresis since their discovery in 2004 [12].Techniques include hydrothermal treatments, pyrolysis, electrodeposition, laser ablation, arc discharge, and others were applied. The characteristics of the hydrothermal method—one pot, straightforward, low temperature, and low cost—make it the best of the three. CQDs have already been produced using a number of precursors.

At low specific density, multi-walled carbon nanotubes (CNTs) have a high surface area (200-400 m2/g), good chemical resistance, elasticity, and strength. Carbon nanotubes have piqued the interest of many potential applications due to their unique structure and mechanical and chemical properties, including nanoelectronics, sensors, electrochemical energy storage, and nanocomposites[13].Developing polymeric nanocomposites filled with CNTs is a promising direction among these applications. This method allows for new materials with

enhanced mechanical properties and electrical conductivity [14].

Covalent or noncovalent functionalization of the nanotubes in the polymer significantly improves dispersion, which can enhance solubility or compatibility. Furthermore, the interaction at the polymer-nanotube interface had a significant impact on the mechanical, thermal, and conductive properties of the Composite [15]. As a result, extensive research is being conducted on the surface modification of carbon nanotubes, primarily to improve their compatibility and dissolubility properties [16]. In this paper, we used a stainless steel autoclave reactor lined with a Teflon chamber to synthesize Carbon Quantum dots, then adding them as a compound to MWCNTs prepared similarly. The x-ray diffraction (XRD), transmission electron microscope (FESEM), and Fourier transformation infrared (FTIR) techniques are used to characterize the prepared MWNTs with CQDs (FT-IR). To form thin films with electrical properties, the dispersed MWCNT mixed with a quantum dot is cast on an ITO glass slide.

2. Experimental section

2.1. Materials and devices

Sodium Hydroxide was purchased from (Romil-SATM); PEG was purchased from (Himedia Wt.: 3300-4000). Deionized Water and Ethanol (99.9%) were purchased from (Scharlau).

The hydrothermal reaction uses an autoclave chamber lined with a Teflon chamber of size 100 ml. A temperature-controllable electric oven provides the heat for a chemical reaction. They are measuring electrical properties, which consists of several parts a device for voltage and current type Fluke(8800), a Lab view for two probe temperature dependent (I-V) characteristics for MWCNT with CQDs thin films. The X-ray diffraction pattern is recorded by device type Philips (PW 1730), and the image of MWCNTs with CQDs is taken by FESEM type TESCAN (Mira3, Czech Republic).

2.2. Synthesis of CQDs

The CQDs were synthesized by using the hydrothermal method. It is prepared by mixing 2g of (PEG; Wt. (3300-4000)) with 3.5g of NaOH pellets in a mixture of 15ml deionized water and 35ml ethanol. The mixture was conducted respectively in a magnetic stirrer for 30min sonicated in an ultrasonic bath for 30min. The above processing scheme confirms that all materials are mixed carefully with each other. The resulting homogenous mixture was transferred into a 100ml stainless steel autoclave reactor lined with a Teflon chamber. The reactor was kept under 160^{o}C in an electric oven for 16

hours. The reactor is left in the open air to cool naturally. The resulting dark brown solution in the Teflon chamber was washed and filtered with ethanol and distilled water several times [17].

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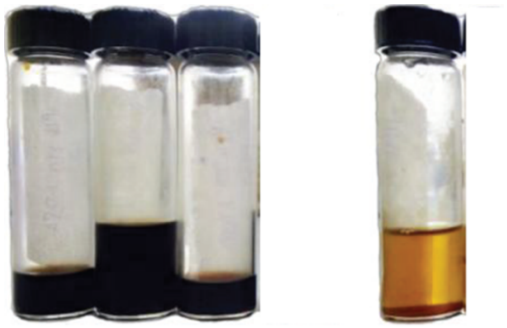
Fig (1): Synthesis of CQDS from PEG by Hydrothermal method.

2.3. Synthesis MWCNTs – CQDs solution

We take 0.5mg of the multi-walled carbon nanotube, which has been previously prepared as a part of ongoing research. By dissolving it with ethanol, it was placed on the magnetic stirrer for 3 hours. It was added with the Quantum Dot solution prepared as described in the above method by mixing it with different weight ratios, as shown in table (1), where it is also placed on the magnetic stirrer for one hour at room temperature. After that, we prepared the films to measure the electrical properties**.**



Fig(2):(a)MWCNTs with CQDs Nanocomposite, and (b) CQDS Sample.

Table (1): The MWCNTs conducting CQDs mixtures solutions

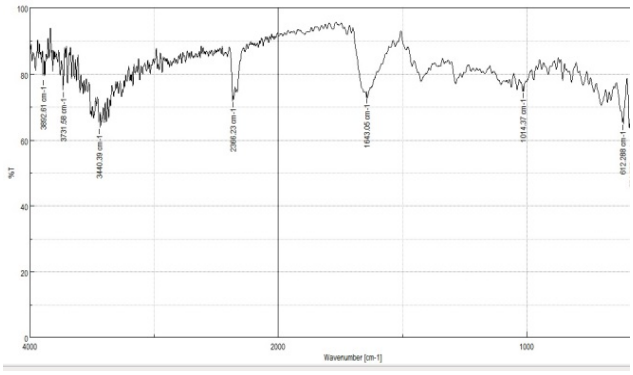
Sample	MWCNTs(Wt.)	CQDs(Wt.)
1	75%	25%
2	50%	50%
3	25%	75%

3. Results and Discussion

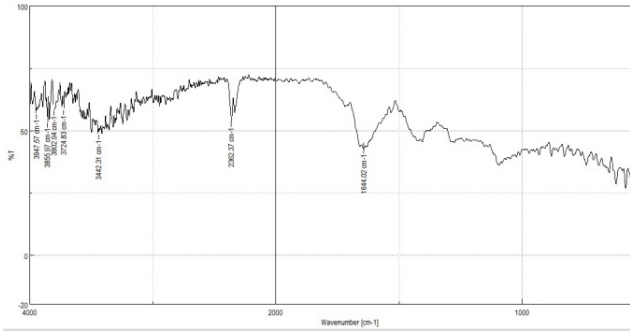
3.1. FT-IR

FT-IR spectroscopy is one of the fundamental tools to reveal the functional groups in the material, especially the organic compounds. Figure 3(a) shows the transmission spectrum of prepared MWCNTs doped with the quantum dot. Many peaks characterize the active functional group present in carbon nanotubes. These groups included carboxyl and hydroxyl,

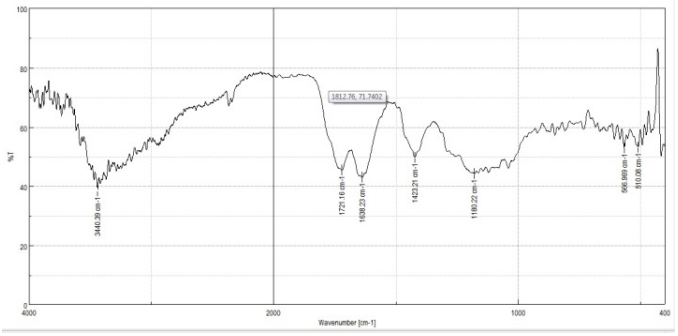
and another group. Table (2) summarizes the most peaks belonging to MWCNTs with CQDs by (75:25%, 50:50% and25:75%). As for the figures (b) and (c), new peaks are emerged, and some of them disappeared, in addition to some shifting in the peak frequency and increase or decrease in peak intensity. This change can be attributed to the doping process with agents, which make some impact on the surfaces of CNTs, as well as due to oxidation [18], [19].



(a)



(b)



(c)

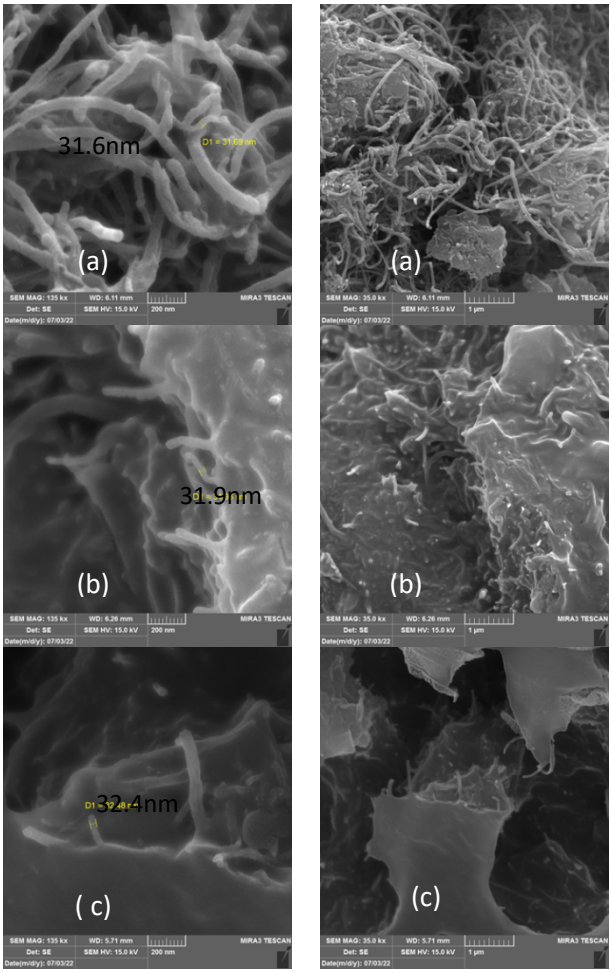
Fig (3): FT-IR spectra of MWCNTs Nanocomposite with CQDs, (a) 75:25 %,(b). 50:50%, (c).25:75%

Table (2): Functional groups for prepared MWCNTs Nanocomposite with CQDs.

Functional group	MWCNTs / CQDs bands(cm-1) 75:25%	MWCNTs / CQDs bands(cm-1) 50:50%	MWCNTs / CQDs bands(cm-1) 25:75%
O-H stretch	3892.6, 3731.5	3947.5, 3855.9, 3802.9 3724.83	
C-H stretch			
C=O stretch	2366.23	2362.37	1721.16
C=C Conjugate	1643.05	1644.02	1638.23
CH_2, CH_3			1423.21
C-O stretch			1180.22
C-O-C Vibration	1014		
C-N aromatic	612.288		
C-O (band)	574.68, 548.649 521.65 462.83	540.93 468.61 407.87	566.969 510.08

3.2. FE-SEM

Figure (4) shows the typical FESEM images of MWCNTs/CQDs nanocomposites prepared by the hydrothermal method. In Fig. 4(a), the walls are composed of graphite sheets aligned to the tube axis. The structures of individual MWCNTs are central hollow, with an outer diameter of 31.69nm, with a small percentage of CQDs particle agglomeration in the form of dots on the walls of the tubes which is the size (8nm), so the MWCNTs ratio is higher than CQDs As for figure.4 (b), it is shown that CQDs nanoparticles have grown as a thin Nano sheet film layer on the surface of the MWCNTs because the diameter of the outer tubes increases a few tens in nanometer. It is around 31.96nm [16]. In Figure 4(c), we notice the immense growth of CQDs particles on the surface of the nanotubes, where these particles are of disk-like sizes and shapes, as it has a wide distribution with a size of (4nm). We also notice an increase in the outer tube diameter, about 32.48nm. We conclude through FESEM characterizes that the CQDs particles that were prepared with MWCNTs compound have a different size distribution ranging from 8nm to 10nm, which is consistent with many kinds of research [20],[21],[29]. We also note that adding carbon quantum dots to nanotubes has enhanced their appearance with few impurities due to the preparation method and the raw materials used.



Fig(4): FESEM image of MWCNTs with Nanocomposite CQDs (a)75:25% (b). 50:50% (c) 25:75%.

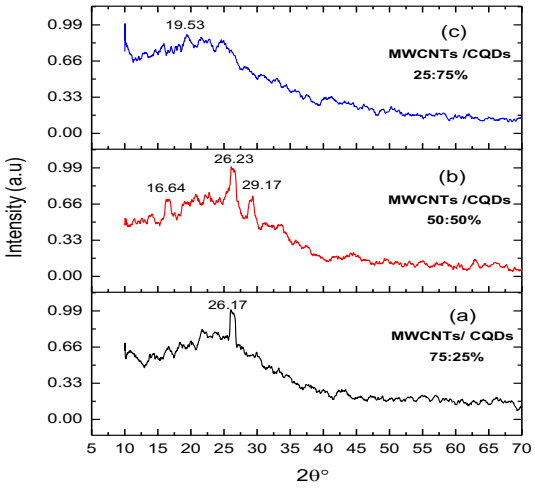
3.3. X-ray diffraction.

X-ray diffraction was used to investigate the crystalline nature and latticed spacing of the current MWCNTs powder composite with CQDs. The crystallite size can also be calculated using Scherer's equation, which is given by the following formula [22][31].

$$D = k\lambda / \beta_{hkl}\, \theta_{hkl} \qquad (1)$$

Where **K**= 0.9 is the shape factor; **λ** =1.5406 Å is the wavelength of x-ray radiation, βhkl half-width at full maximum (FWHM) of the diffraction band (in radians); θhkl Bragg- diffraction angle (peak position in radians).

Figure (5) shows the XRD pattern of the MWCNTs composite with CQDs prepared by the hydrothermal method. In Figures 5a and 5b, the broad peaks within the band appear (2θ=26.17A.26.23A, 29.17A) due to the presence of MWCNTs in a high percentage, while the dominant peak is usually 26.23. This peak can attribute to graphitic carbon structures, which disappear as the percentage of doping increases with CQDs[23], while in figure 5c, the main and dominant peak (2θ =19.53A), this peak can attribute to CQD structures.[28] The grain size for each peak can be calculated from equation (1) described in table(3). This indicates that the crystal structure of CQDs is graphite, but the distance between the atomic levels is larger than that of bulk graphite. The reason is due to the distribution of functional groups on the surface with a large area, Which leads to the generation of functional groups rich in oxygen; similar results have been reported [24][25].



Fig(5): XRD patterns for prepared MWCNTs Nanocomposite with CQDs.

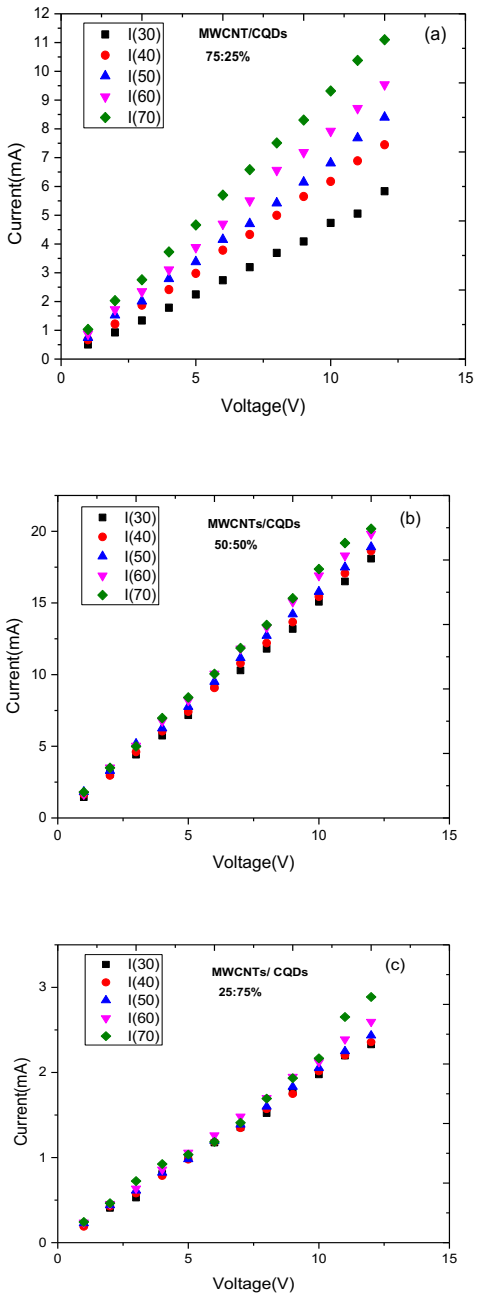
Table(3): Grain size of MWCNTs Nanocomposite with CQDs.

MWCNT /CQDs	Pos [2T]	d-spacing (Å)	FWHM [2T]	G.S (nm)
75:25%	26.17	3.42	22.8938	0.3561
50:50%	16.64	5.33	8.952	0.877
	26.23	3.40	8.952	0.863
	29.17	3.08	8.952	0.858
25:75%	19.53	4.66		

3.4. Electrical properties

Determining the mechanics of electrical conduction in materials depends on studying the characteristic (I–V Characterization) and studying the effect of heat on the conductivity of the prepared films. There may be more than one conduction mechanism, depending on the thickness of the prepared film, the strength of

the applied electric field, or the temperature [26].



Fig(6): I-V Characterization for MWCNTs film Nanocomposite with CQDs.

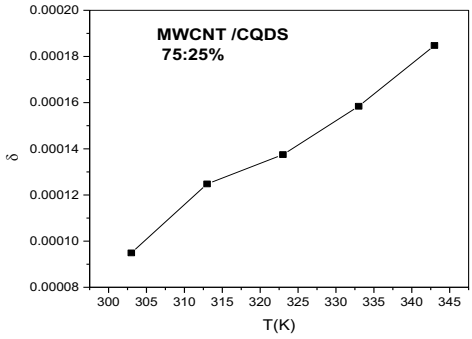
Figure (6) shows the current and voltage characteristic of MWCNTs with CQDs at different temperatures. We note from the figure that the current increases linearly with the increase of the voltage applied to the film for all applied voltages, and this reflects the ohmic behavior of these films. We also note that the current increases with increasing temperature, Which indicates that the material behaves like a semiconductor and is based on the current and voltage values in figure (6). The electrical conductivity is calculated from equation (5)[27][30].

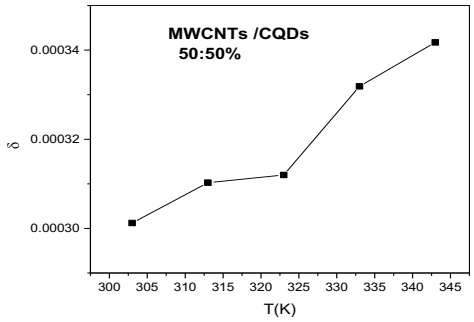
$$\dot{O}= \frac{I}{V} \quad \frac{S}{Wd} \qquad (2)$$

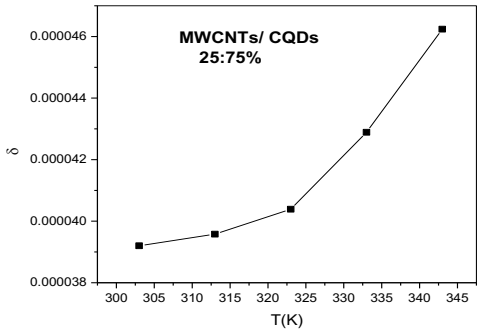
I: Current, V: Voltage applied on both ends of the pole, S: pole length, d: film thickness, W: the distance between the electrodes. The electrical conductivity of the three samples was calculated from Equation(2),where we notice from Figure(6.a,b,c) that the conductivity increases with the increase in the weight ratios of the CQDs, and we note a decrease in the activation energy of films with the increase in the weight ratios of the CQDs. The conduction mechanism is jumping. The distance between the particles is such that an electron jump can occur. The increase in conductivity can be explained by the emergence of pathways as a result of the accumulation of CQDs inside MWCNTs material or the formation of

conductive regions and is carried out by jumping.

3.4.1. The effect of temperature on electrical conductivity







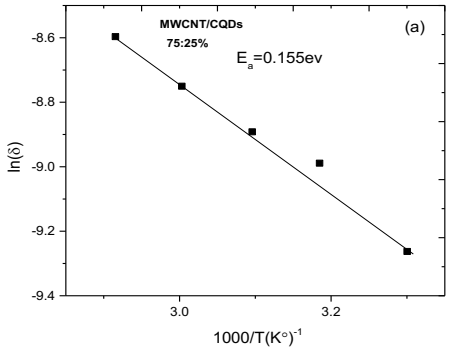
Fig(7): the change of conductivity of the prepared films with temperature.(a).75:25%, (b).50:50%, (c).25:75%

We notice from figure(7) that the conductivity increases exponentially, indicating that the models behave like semiconductors. The electrical conductivity can be described using the arenius exponential equation, which is given by the following formula [28]:

$$\sigma = \sigma_0 \exp^{Ea/K\,T} \qquad (3)$$

Ea: activation energy, K.B.: Boltzmann constant, T: absolute temperature, σ: electrical conductivity.

By drawing the relationship between the logarithm of electrical conductivity and temperature and using the above equation, the activation energy can be calculated using the slope of the straight lines. Figure (8) represents the relationship between In (σ) and (1000/T) for MWCNTs film Nanocomposite with CQDs.



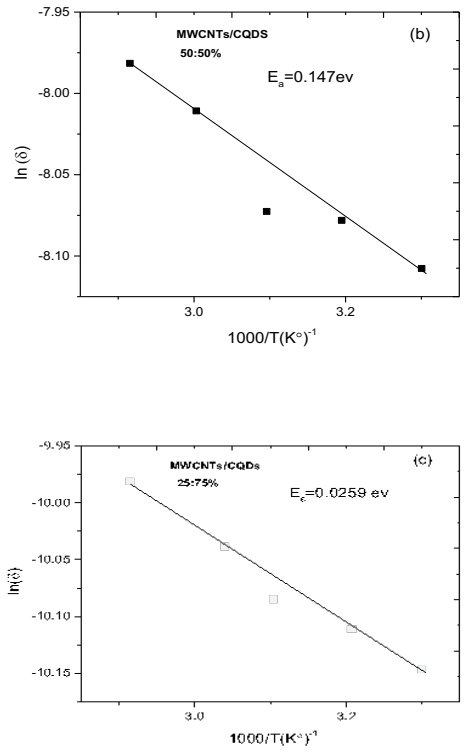


Fig (8): relationship between In(σ) and 1000/T for MWCNTs film Nanocomposite with CQDs.(a).75:25%,(b)50:50%,(c)25:75%

Table (4): Electrical Conductivity and activation energy for MWCNTs/CQDs Nanocomposite at room Temperature.

MWCNT /CQDs	75:25%	50:50%	25:75%
E_a(ev)	0.155	0.147	0.0259
Ơ(S/cm) At 300K	$1*10^{-4}$	$3.01*10^{-3}$	$3.9*10^{-3}$

4. Conclusion

In this study, the CQDs were synthesized by hydrothermal method using (PEG) at (160℃). Then, it was added to the carbon nanotubes prepared in the same method using Ferrocene as carbon precursor and Sulfur and sodium hydroxide pellets as oxidized and reduction agents, respectively, at 200℃. The result of FESEM appeared to be the presence MWCNTs with CQDs, where spherical particles with different size distributions ranging from 8nm to 10nm and carbon tubes with different outer diameters from 31.69nm to 32.48nm. The presence of various functional groups in synthesized MWCNTs with CQDs is confirmed by FTIR analysis, good electrical conductors, and activation energy (0.155ev, 0.014ev,0.00259ev). The future aim of this study is to make Composite with other materials to modify new materials to employ them in some applications, including Sensors, Solar cells, Biological applications, Medical Imaging applications, Materials Science applications, and Supercapacitor.

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