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Comparative Study of Multi-Walled Carbon Nanotube Properties Before and After Purification Prepared at Low Temperature

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Abstract. This study includes the preparation of multi-walled carbon nanotubes (MWCNTs) by hydrothermal method at temperature about 200° C. The starting materials are ferrocene and sulfur with sodium hydroxide as a reducing agent. The purification process of prepared MWCNT is carried out by using nitric and sulfuric acids as long as hydrogen peroxide and acetone. The structural and optical properties of MWCNTs are investigated by the FT-IR, TEM, XRD and UV-VIS characterization techniques. The d-spacing is 3.42 Å from XRD, the bandgap about 4eV to 3.7eV from optical calculation, the average ID and OD are respectively, 34nm and 52nm from TEM measurements with the length of (0.7-1)µm.

Keywords: Multi-walled carbon nanotube, hydrothermal method, Treatment, Purification.

INTRODUCTION

The nanomaterials and nanoscience now become a common word not only in scientific research community but also in our daily life. Accidentally, in 1991 Carbon nanotubes are discovered by Sumio Iijima [1]. However, in 1997 The Journet and his group prepared carbon nanotubes using the arc discharge method [2]. In 2000 Kokai et al. also used pulsed lasers to produce SWCNTs [3]. In 2010 Campos-Delgado et al. prepare CNTs using chemical vapor deposition method [4]. In the same year the Sahebali and his group prepared MWCNTs by hydrothermal method using polymer (PEG) [11]. In 2011 Youn and his group prepared CNTs by microwave interaction [5]. However, the discovery Iijima in 1991, remains of special importance because it consider as a starting point in a new nanotechnology era. The scientific community takes a special attention to CNTs, Due to its potential application in all fields, such as, Paper batteries, strengthening metal, drug delivery, dielectrics, gas sensors, films, ultra-capacitors, polymers, solar cells, thermal managements [6]. Various form of carbon nanomaterials are fullerene, single wall and multiwall carbon nanotubes, carbon nanofibers, carbon nanohorns, carbon nanocapsules, carbon nanooxonion, carbon nanospheres, ferromagnetic filled CNTs, carbon nanosheets, etc. have been prepared by using different techniques [7]. The synthetic methods of previous different structures are included: Arc discharge, Laser vaporization, Pyrolysis, high pressure catalytic decomposition of carbon monoxide, flame synthesis, Chemical vapor deposition (CVD), Plasma enhanced CVD, electrophoretic decomposition and low temperature hydrothermal method [8]. The main drawback of the most preparation methods are low yield, required high temperature, expansive, difficultly technical handling, in addition to it needed post treatment for purification and functionalization of carbon nanostructure product before using it in a various applications[9].

The CVD and its different versions have been used widely to prepare most the CNTs for laboratory and industry aims. On the other hand, the method like hydrothermal is attractive because it is a low temperature, it use an ecofriendly starting materials, and technological low cost when compare with other methods [10]. The important steps for CNTs after preparation are purification and functionalization, both are necessary to removal starting

materials impurities present with product CNTs and to modified the outer surfaces to attach foreign material or filling the CNTs with it to enhancing its properties [11].

There are many procedure have been used to purification the CNTs by applied a different agents, such as hydrochloric, nitric and sulfuric acids, in addition to the hydrogen peroxide, acetone, etc. [12,13]. The microwave, heat, and mechanical stirring also have been used along with previously chemical agents.

In the present paper, we will synthesis a multi-walled carbon nanotube by hydrothermal method by using stainless steel autoclave reactor lined with Teflon chamber. The prepared MWNTs are characterized by x-ray diffraction technique (XRD), transmission electron microscope (TEM), Fourier transformation infrared technique (FT-IR), ultraviolet-visible-near infrared spectroscopy. For optical properties the dispersed MWCNT is casting on glass slide to formed thin films.

Experimental section

Materials and devices

Ferrocene (98%) and Sulfur both purchase from Aldrich; Sodium Hydroxide purchase from (Romil-SATM); Deionized Water and Ethanol (99.9%) purchase from (Scharlau); sulfuric, hydrochloric, Nitric acids from(Scharlau) and hydrogen peroxide and acetone(99%9) from(Scharlau)

Autoclave chamber lined with Teflon chamber of size 100 ml is used for hydrothermal reaction. The heat for chemical reaction is provide by temperature controllable electric oven. The shimadzu spectrophotometer type 4200 is to record optical spectra for MWCNT thin films. X-ray diffraction pattern is record by device type Philips (PW 1730), the image of MWCNTs is take by TEM type Philips (CM30, Netherlands V=200KV).

Synthesis of MWCNTs

The CNTs is synthesized by using the hydrothermal method. The procedure is modified depended on the other workers [14]. Briefly, the weighing ratio equal (1:2) of both ferrocene and sulfur were dissolved in a mixed solution of 15ml deionized water and 35ml ethanol with 3.5g of NaOH pellets. The ferrocene acts as a source of carbon and the element sulfur as catalyst while the hydroxide acts as a reducing agent .The mixture was conducted respectively, in a magnetic stirrer for a one hour, sonicated in an ultrasonic bath for 45 minutes, and then stirred again for 30 minutes. The provisos processing scheme to confirm that all materials are mixed carefully with each other. The resulting homogenous mixture was transferred into 100ml stainless steel autoclave reactor lined with Teflon chamber. The reactor kept under 180- 200 $^{\circ}$ c in electric oven for 24 hours. The reactor is left in open air to cool naturally. The resulting black precipitate in Teflon chamber was washed and filtered with ethanol and 0.1 HCl followed by distilled water until PH reach to 7 of washing solution. Then the black solid was separated and collected from solution subsequently dried at 60 $^{\circ}$ c for 10 hours in an electric oven.

PURIFICATION OF MWCNTS

Step (1)

In this treatment, 0.02 g of raw MWCNTs was treated in mixture of HNO₃ and H₂SO₄ 1:3 in a flask. Then the mixture was ultrasonic for one hour, at that time placed on the stirrer for 9 hours at for 60 $^{\circ}$ c, next is added dilute hydrochloric acid for 2 hours. Then the solution was washed with ethanol and distilled water several times, hence the black solid was separated and collected from solution and leave to dry at 50 $^{\circ}$ c for 10 hours in the oven [15, 23].

Step (2)

There are two ways to purify MWCNTs. The first is an oxidation with H₂O₂, while the second one consists of an oxidation with H₂O₂ followed by acetone treatment. 0.01g of purified MWCNTs (from step I) was added to 50ml of

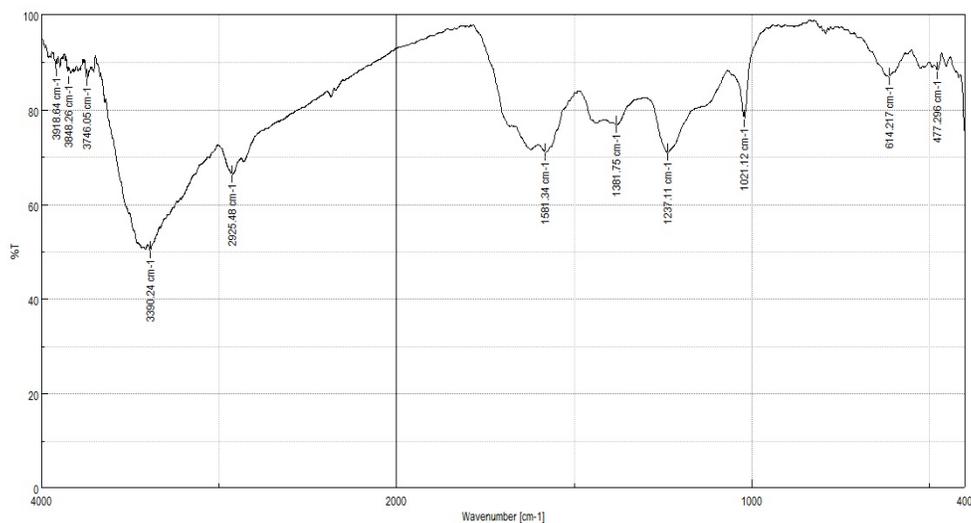
H₂O₂ and sonicated 1.5 hour. The mixture was left in a refrigerator for 24 h, after that, the solution allowed to warm to room temperature then heat gradually to 50C until all hydrogen peroxide was completely destroyed. Finally, the sample was washed with deionized water and dried at 80C for 4 h. The second route is carried out by the same steps except after oxidation process with H₂O₂ is completed, the dried sample is dispersed in 15 ml of acetone and sonicated for 15 min. The suspension was then centrifuged for 15 min. The separated CNTs were then calcined at 100C for 2h [16].

RESULTS AND DISCUSSION

FT-IR

FT-IR spectroscopy is one of the fundamental tools to reveal on the functional groups in the material, especially the organic compounds. The FT-IR spectra of before and after treatment are shown in figure 1a and 1b respectively. We note from the figure 1(b) that there are carboxylic functional groups on the surface MWCNTs treated.

The figure 1(a) shows the transmission spectrum of prepared MWCNTs before treatment. There are many peaks that characterize the active functional group present in carbon nanotubes. These groups are included carboxyl and hydroxyl and other group. The Table (1) summarize the most peaks belonging to MWCNTs before and after purification process. There are a new peaks emerging after treatment and some of them disappeared, in addition to there are some shifting in the peak frequency and increase or decrease in peak intensity. These changing can be attributed to the processing with agents which make some impact on the surfaces of CNTs and also oxidation occur simultaneous.



(a)

FIGURE 1. (Continued)

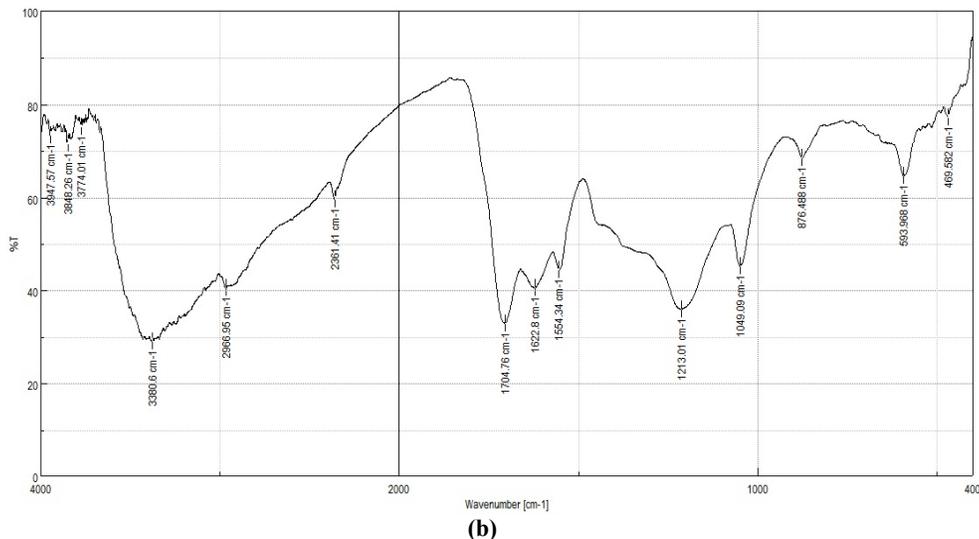


FIGURE 1. FT-IR spectra of MWCNTs (a) before, (b) after purification.

TABLE 1. Functional groups for prepared MWCNTs.

Functional groups	Before purification cm-1 peak	After purification cm-1 peak
C = H (stretch)	3918.64,3848.26,3746.05	3947.57, 3848,26, 3774.01
O – H (stretch)	3390.24	3380.6
C –H (stretch)	2925.48	2966.95
C=O (stretch)		1704.76
C = C (aromatic)	1581.34	1554.34
C – C (aromatic)		1622.8
C –O –C	1381.75	
C-C (stretch)	1237.11	
C-O (stretch)	1021.12	1213.01
C-H bend (ortho)		1049.09
C-H (aromatic)	614.217	876.488
C-O bend	477.296	593.968,469.582

TEM

The TEM images of MWCNTs are shown figure 2. The images before treatment clearly show that the prepared MWCNTs contained or covered with a reasonable amounts of impurities back to starting materials. While the image in figure 2d and 2c that undergone to double purification treatment have no impurities which indicate that this type

of the treatment processes are very successfully and played imported role to obtaining clean nanotubes in the hydrothermal procedure using ferrocene as a raw materials . The outer diameters ranging from 48 to 52 nm and the inner from 15 to 34nm. The MWCNTs lengths within (0.7 to 1) μm estimated from TEM measurements. The post treatment of MWCNTs leads to functionalization of the outer surface of tubes and also leads to narrowing the radius of CNTs [20].

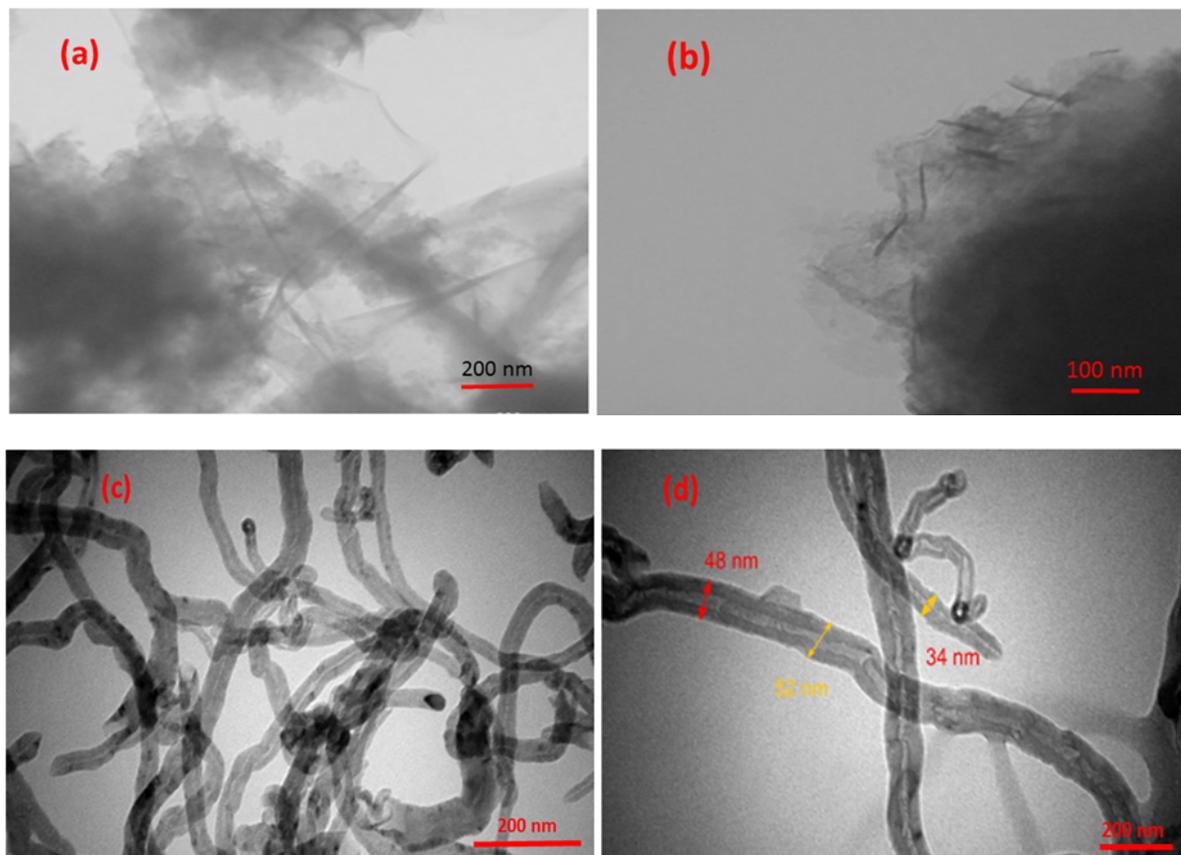


FIGURE 2. TEM image of MWCNTs before (a,b) and after (c,d) purification.

X-ray diffraction.

The crystalline nature and lattice d-spacing of the current MWCNTs have been investigated by using the X- ray diffraction technique. The interlayer or d-spacing of present MWCNTs is 3.42 \AA for (d200 plane), this value is consisted with a reported value for MWCNTs [17]. The crystallite size also can be calculated from XRD pattern by using Scherer's equation, which is given by the following formula [18]:

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

Where $K = 0.9$ is the shape factor; $\lambda = 1.5406 \text{ \AA}$ is the wavelength of x-ray radiation, β_{hkl} half- width at full maximum (FWHM) of the diffraction band (in radians); θ_{hkl} Bragg- diffraction angle (peak position in radians). Figure (3a.b) shows the XRD pattern of the MWCNTs powder prepared by hydrothermal method before and after treatment process. In figure 3a, the pattern have many diffraction peaks, ($2\theta = 23.211, 26.076, 27.875$). These peaks can attribute to graphitic carbon structures [18]. The grain size for each of these peaks can be calculated from equation (1), ($D = 25.69 \text{ nm}$) [19]. After the post treatment, some peaks are disappeared and the crystal structure is modified (fig.3b), also the main peak ($2\theta = 26.1593$) is became wider compared with previous (before treatment). This effect resulting of purification with H_2O_2 and acetone, which removes all organic residues and also make oxidation, similar this results have been reported [20].

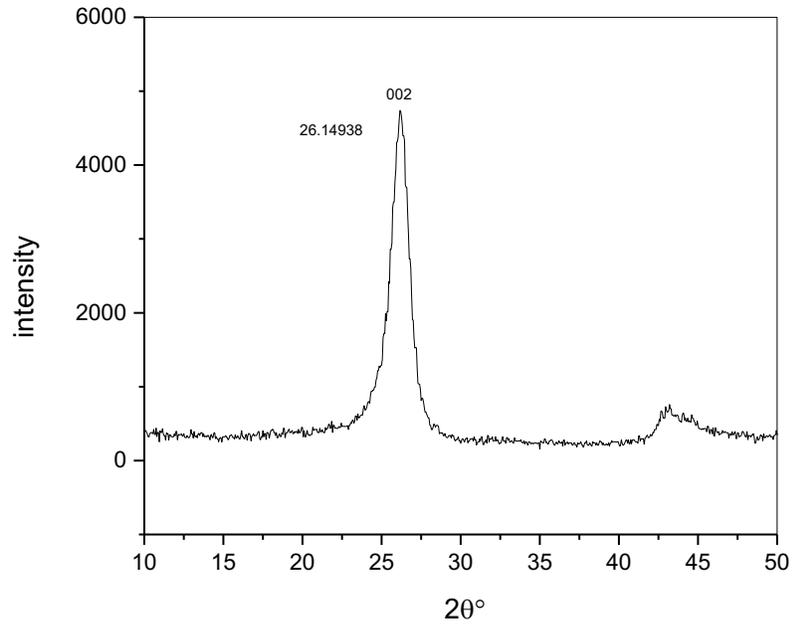
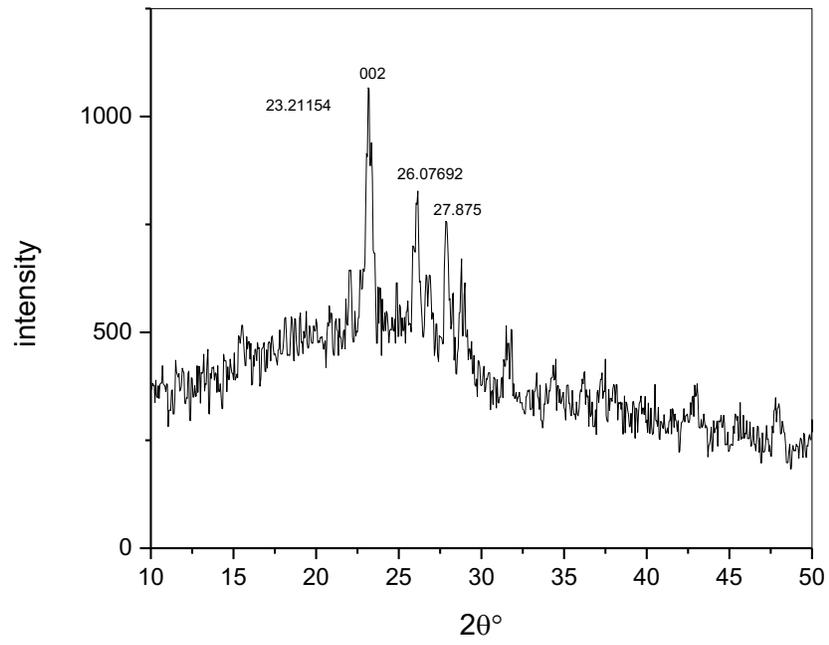


FIGURE 3. XRD patterns for prepared MWCNTs before (a) and after (b) purification.

Optical Properties

Absorption coefficient of MWCNTs film

The absorption coefficient (α) of the (MWCNTs) films in the basic absorption region was calculated by means of the absorbance (A) for thin films of thickness (d) using the relationship:

$$\alpha = \frac{2.303}{d} A \quad (2)$$

As a result, there is no way to determine the value of the reflectivity. Several methods have been used to correct the reflectivity. One of these methods is done by drawing a straight line of large wavelengths towards small wavelengths for the purpose of determining the amount of correction in absorbance (A), and then subtracting this value from the absorbance values (A) corresponding to other wavelengths. Figure (4) shows the reflectivity correction of MWCNTs films before and after purification.

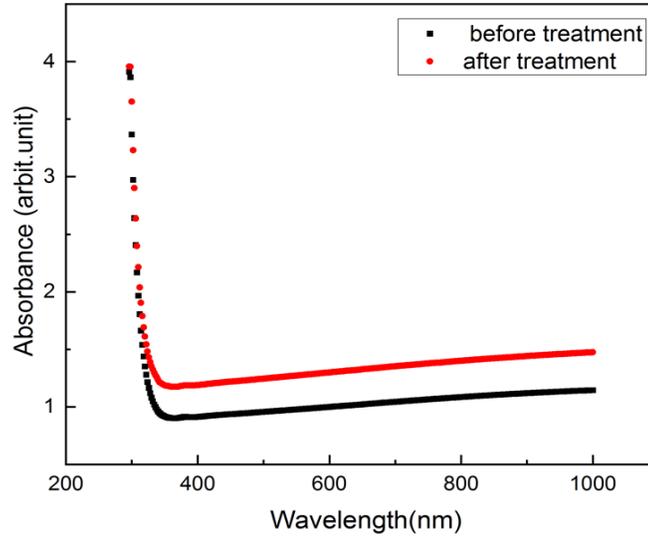


FIGURE 4. Optical Absorbance for MWCNTs film before and after purification.

The value of the absorption coefficient is what determines the type of electronic transitions that occur inside the solid. When the value of the absorption coefficient (α) is greater than 10^4cm^{-1} , this means that the transition is direct as the electron moves from the top of the valence band to the bottom of the conduction band with the wave vector itself (k) i.e. ($\Delta k=0$), which means that energy and momentum are conserved, The relationship between the absorption coefficient and the gap energy is represented by the following formula [21]:

$$\alpha = \alpha_o \frac{[h\nu - E_g]^r}{h\nu} \quad (3)$$

α is a constant quantity that depends on the type of substance; E_g is the energy gap. Either r is a fixed quantity and its magnitude ($1/2$ for the direct allowed transition and $3/2$ for the direct forbidden transition).

But when the value of (α) is less than 10^4cm^{-1} , this means that the transition is indirect and the electron moves from the top of the valence band to the bottom of the conduction band for different values of the wave vector (k), meaning that ($\Delta k \neq 0$) and this means that the momentum is not conserved, so to keep momentum conserved, the process is accomplished by the emitted or absorbed of phonon. in this case, the relationship between the absorption coefficient and the indirect gap energy is determined by the following formula[22]:

$$\alpha = \alpha_o \frac{[h\nu - E_g^i \mp E_p]^p}{h\nu} \quad (4)$$

E_p is the energy of the phonon accompanying the indirect transmission process.

E_g^i / Indirect gap energy. p is a constant quantity of (2) for the indirect allowed transition (3) for the indirect not allowed transition.

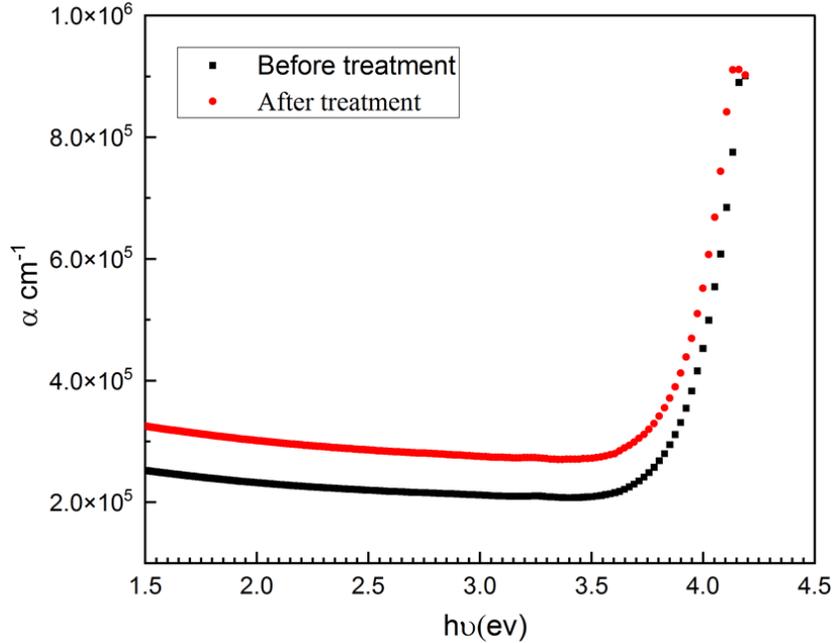


FIGURE 5. shows the relationship between the absorption coefficient and photon energy of MWCNTs films before and after purification.

We can note from the figure (a,b) the values of the absorption coefficient are more than 10^4 cm^{-1} this indicates an direct transition for the prepared MWCNTs films.

Energy gab calculation E_g

Figure (6) shows the relationship between $(h\nu\alpha)^2$ and the photon energy of MWCNTs film according to the relationship (3). The energy gap was calculated from the extrapolated of the straight line with $h\nu$ and it was about (4 eV) and (3.7 eV) for films before and after purification respectively. We noted the lowering of optical bandgap due to the oxidation of MWCNTS during the purification process. This effect can be attributed to decreasing in the size of CNT. The values of energy gaps indicate that the types of films are semiconductors.

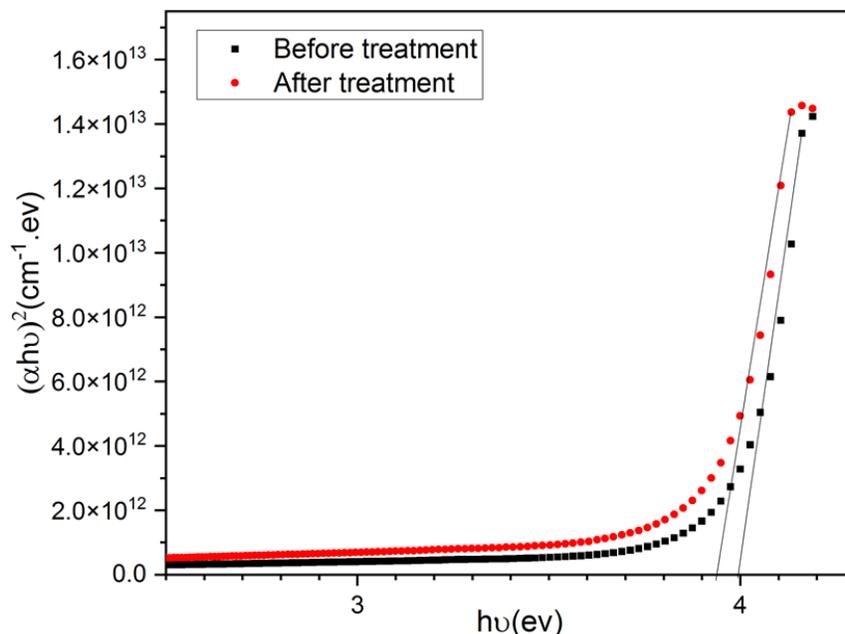


FIGURE 6. the relationship the $(\alpha hv)^2$ and energy photon for MWCNTs films before and after purification.

CONCLUSION

The carbon nanotubes synthesized by hydrothermal method using Ferrocene as carbon precursor and Sulfur and sodium hydroxide pellets as oxidized and reduction agents respectively at 200°C. The XRD pattern revealed that formed MWCNTs are polycrystalline nature with d-spacing equal to 3.42 Å. The result of TEM appeared that the post treatment step is very important and there are remarkable changes between the appearance and the size of MWCNTs before and after treatment. The presence of various functional groups in synthesized MWCNTs is confirmed by FTIR analysis. The values of bandgaps (3.7-4eV) of MWCNTs thin films indicated that these films have a semiconductor nature. The future aim of this study, we will be making composite with other materials to modify the pristine material to employ it in some applications including Sensors (gas, optical sensor), Solar cells and Supercapacitor.

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