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Functionalization of single and multi-walled carbon nanotubes by chemical treatment

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Abstract

In this work we experimentally investigated SWCNTs and MWCNTs to increase their thermal conductivity and electrically functionalization process using different reagents (nitric acid, HNO_3 followed by acid treatment with H_2SO_4), then washed with deionized water (DW) and then treated with H_2O_2 via ultrasonic technique. Then repeated the steps with MWCNTs and compare their results in an effort to improve experimental conditions that efficiently differentiate the surface of the single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs) that less nanotubes destroy and to enhance the properties of them and also to reduce aggregation in liquid. the results were prove by XRD, and infrared spectroscopy (FTIR). The FTIR spectrum shows the presence of carboxylic group after treatment with (acid oxidation and H_2O_2) and refers to Functionalization (SWCNTs) and (MWCNTs) on the surface wall microscopic images show surface adjustment on SWCNTs and (MWCNTs) structure after any treatment. AT last, a fully of SWCNTs and MWCNTS were obtained successfully accomplished with the reduction of the collapsed structure.

Key words

Multi-walled carbon nanotubes (MWCNTs), H single-walled carbon nanotubes (ESWCNTs), functionalization.

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تحسين خواص الانابيب الكاربونية النانوية المفردة والمتعددة الجدران بطريقة المعالجة الكيميائية

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الخلاصة

في هذا العمل قمنا بالتحري عن عملية تحسين وظائف SWCNTS، والتي يتم معالجتها بمواد تفاعلية مختلفة (حمض النيتريك، HNO_3 وتليها المعالجة الحمضية باستخدام H_2SO_4)، ثم تغسل بالماء المقطر (DW) ثم تعامل مع H_2O_2 عبر تقنية الموجات فوق الصوتية. ثم كرر الخطوات مع MWCNTs وقارن نتائجها في محاولة لتحسين الظروف التجريبية التي تفرق بكفاءة سطح الأنابيب النانوية الكربونية أحادية الجدار (SWCNTs) والأنابيب النانوية الكربونية متعددة الجدران (MWCNTs) التي تقل فيها الأنابيب النانوية ولتعزيز خصائصها وأيضا للحد من التجميع في السائل. وقد تم تأكيد النتائج من قبل XRD، والتحليل الطيفي بالأشعة تحت الحمراء (FTIR)، المجهر الإلكتروني الماسح (SEM). ويبين الطيف FTIR وجود مجموعة الكربوكسيل بعد العلاج مع (أكسدة حامض و H_2O_2) ويشير إلى functionalization (SWCNTs) و (MWCNTs) على الجدار الخارجي السطح. تظهر الصور المجهرية تعديل السطح على SWCNTs وبنية (MWCNTs) بعد كل معاملة. وأخيرا، تم الحصول على بئر من SWCNTs و (MWCNTs) بنجاح مع الحد من الهيكل المنهار.

Introduction

Carbon nanotubes (CNTs) are composed of graphene layers which are rolled up cylindrically with diameter in the nanometer scale. CNTs consist fully of sp^2 carbon-carbon bonds and attractive scientists around the world because of its unique structure, electronic and optical properties [1, 2] as well as, CNTS possibly better conductors than metals comparable to Copper at room temperature while, because of the being of different defects or pollution created during the CNTs growth, the conductivities of individual CNTs are much Less than these under ballistic conduction with nanoyubes free of defects [3, 4].

Furthermore, the critical dilemma in using carbone nanotubes is due to the low dispersion and aggregation of carbon nanotubes, as well as the interaction of the attractive van der Waals between them [5]. Improved The dispersion characteristic of carbon nanotubes have become a challenge to increase the characteristic of carbon nanotubes (CNTS). To outdo Self–aggregation, the chemical adjustment of Carbon nanotubes (CNTs) has been known as an effective method of characterization, encouraging dispersion and activating the surface at the same time or using the surfactant is an effective way to improve its adhesion to host matrix material [6-8].

Carbon nanotubes like MWCNTs and SWCNTs have attracted particular attention because their superb mechanical and electronic properties as well as their resistance to acid / base media [9]. These nanoparticles take important role in developing of Sensors [10] and the manufacture of composite materials [11]. However, the static nature and hydrophobic of nanotube surface that have been prepared is unlike to these applications [12]. In order to develop the contact of carbon nanotubes and molecules, it is essential to modify the nanotube surface. Oxygen containing groups are formed which are attractive to develop the interaction between carbon nanotubes and the solvent Matrix on surface of nanotubes by chemical processing such as nitric and sulfide acid [13].

Material and method

1.Material's

Carbon nanotube single wall carbon nanotubes (SWCNTS) and multi wall carbon nanotubes (MWCNTS). SWCNTs are considered as a graphene plate wrapped in a cylinder where they are not defective, with hexagonal rings placed in contact to join smoothly [14, 15]. MWCNTs, referred to as the name, are referred to as many graphene sheets wrapped in carbon nanotubes, filling the inner cavities of each other until the nanotube tube ends. [16] Thus, many layers of MWCNTs were built with SWCNT more solid than [17].

Sulfuric acid (H_2SO_4)

Sulfuric acid has a chemical formula H_2SO_4 is a strong metallic acid. It has a mass of 98.08 g/mol, a colorless appearance liquid, density of 1.84 g/cm^3, melting point 10.38 $^\circ$C, boiling point 279.6 $^\circ$C.

Nitric Acid (HNO_3)

Nitric Acid or Fire Water HNO is a highly toxic, highly corrosive acid that has the potential to cause serious burns and is colorless in its purity. Old samples tend to yellow because of accumulation of nitrogen oxides. Its formula: HNO_3, Particle block: 63.01 g, Density: 1.51 g/cm "Boiling point: 83 $^\circ$C.

Hydrogen peroxide (H_2O_2)

Hydrogen peroxide or oxygen water is a chemical compound with H_2O_2, a light blue color appears colorless in diluted solutions, slightly more viscous than water. Hydrogen peroxide is a weak acid, but it has strong oxidizing properties.

Functionalization method of CNTs

1.Treatment of Single-Wall Carbon Nanotube (SWCNTs)

0.2 g, of (Raw-SWCNTs) was treated in mixture of (25% HNO_3 and 75% H_2SO_4) and sonicated vibrations in the Ultrasonic Bath for 40 min at temperature of 37 °C. Then, the mixture washed with (40) mL of DI water using polycarbonate membrane (0.22 μm). The procedure of treated SWCNTs) was repeated with substituted solvent like 100 % V\V H_2O_2. The subsequent of treatment with H_2O_2 leads to complete the oxidation process initiated by (HNO_3 and H_2SO_4) in a moderate manner. The Solid was washed with deionized water several times until the pH of the filter was about (7). The solid material was dried for 24 h at (170 - 200 °C) producing functionalized SWCNTs with functional groups (SWCNT–COOH) [18].

2. Treatment of Multi-Wall Carbon Nanotube (MWCNTs)

In this treatment, 0.15 g of Raw–MWCNTs was treated in mixture of (25% HNO_3 and 75% H_2SO_4) in a flask. The raw material and acids were ultrasonic in the ultrasound bath at for 50 min at 37 °C. Then, the mixture of was diluted with (40) ml of DI Water using a polypropylene membrane (0.22 mm) in Vacuum –Filtered. Then, the solvent was substituted with H_2O_2 (100%) and the same procedure was repeated by treating with H_2O_2 in a moderate manner. The solids were washed with deionized water until the PH of the filter was about (7) and dried in the furnace for 24 hour at (170 - 200 °C) resulting in functionalized MWCNT-COOH (MWCNT–COOH) [14]. Surface modification of carbon nanotubes (CNTS) using acids can be considered an effective method to overcome these problems. The process of functionalizing different carbon nanotubes with different reagents and varying degree of Oxidation is a process in which functional groups (OH, C =O, and COOH) may be applied to (SWCNTS) and (MWCNTS) as shown in Fig.1 describing Phase oxidation procedures [8].

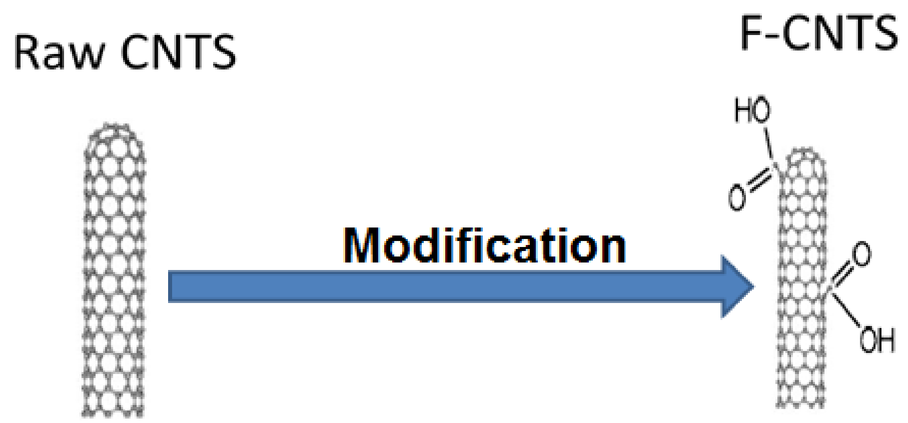


Fig.1: Chemically modified carbon nanotubes (CNTs) [7].

Destruction of the structure has caused changes in the worthy characteristics of the CNTs, This is the main objective at the work. We're studying the dispersion in this research, morphology of functional MWCNTs and SWCNTs as well as the chemical properties with different kinds regents (HNO_3 concentration and H_2SO_4). We are trying to make MWCNTs and SWCNTs with less disruption of the structure, and make comparison F-SWCNT with raw-SWCNT as well as functionalized F-MWCNT by acid treatment as compared with raw-MWCNTs as shows in Fig. 2.

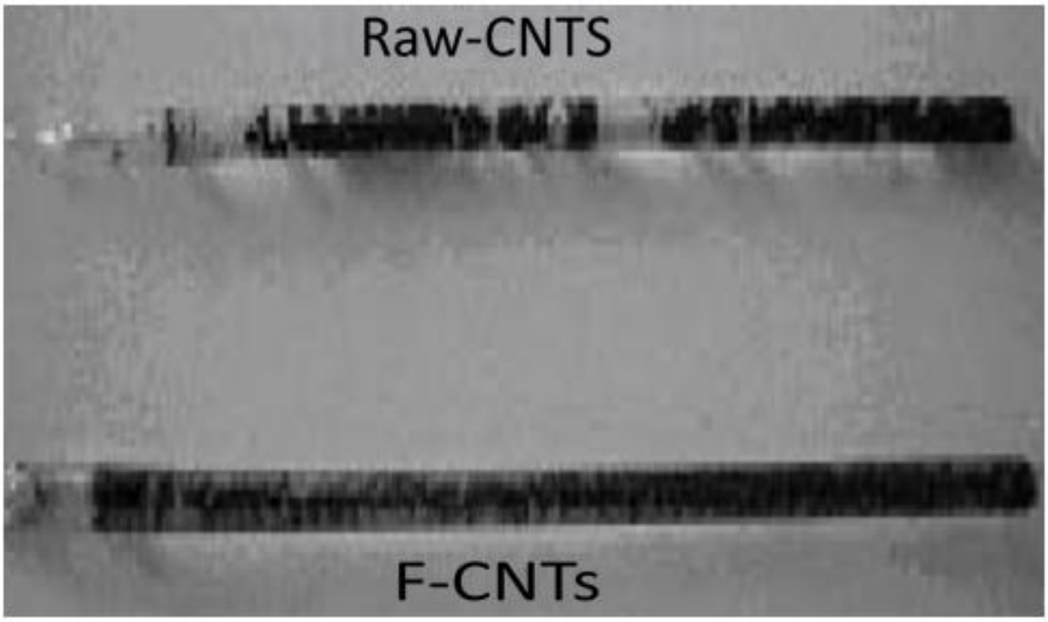


Fig. 2: Carbon nanotubes before and after functionalization.

To estimate the dimensions and crystalline structure (MWCNTs), (SWCNTs) and fictionalized an x-ray diffraction study (XRD) was performed. FTIR is mainly used as qualitative technique for evaluation of functional group [19]. chemical composition. The crystalline structure of functional patterns (CNTs) was confirmed by x-ray diffraction measurements (XRD). The method was use in technical specification CNTs produced a segmented structure towards functional CNTs [19].

Characterization of the functionalized CNTs

The surface treated tubes (CNTs) by various means carboxylic functional groups (O =C–OH and C–OH) can be shown. To complement the dispersion data, chemical structures and detailed structures such as carbon nanotubes (CNTs) and functional nanotubes were characterized by XRD, FTIR and SEM. Of the FTIR spectra, indicates the presence of carboxylic group (CNTs) n the outer surface wall and

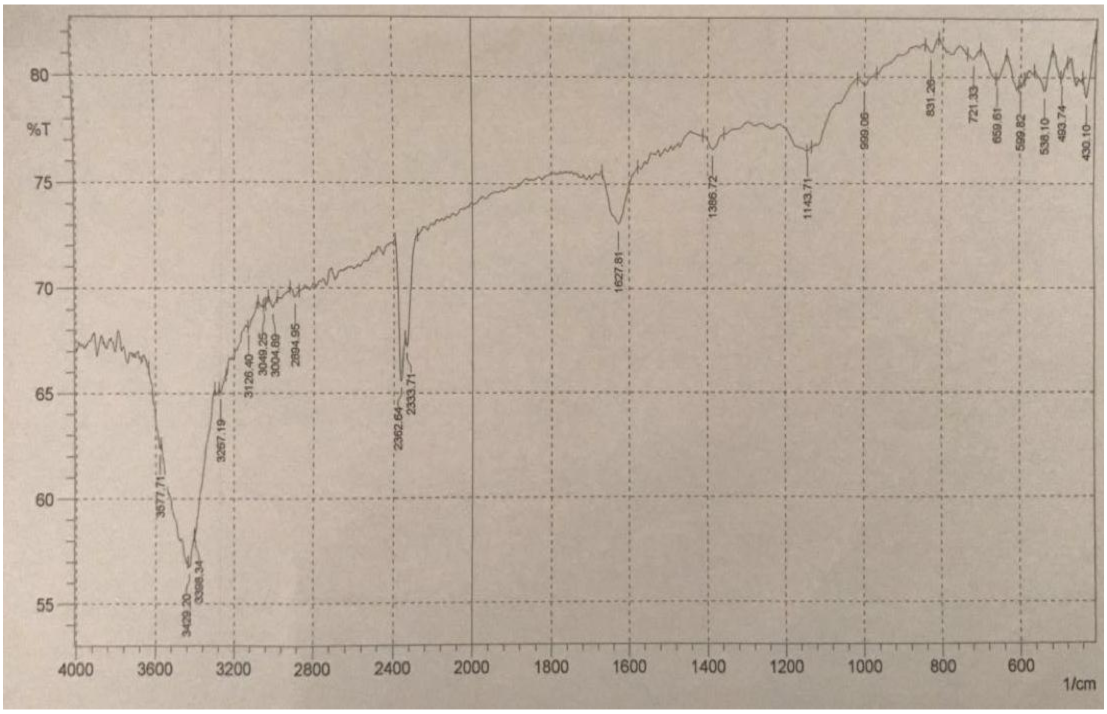
Results and discussion

1. Infrared spectroscopy (FTIR)

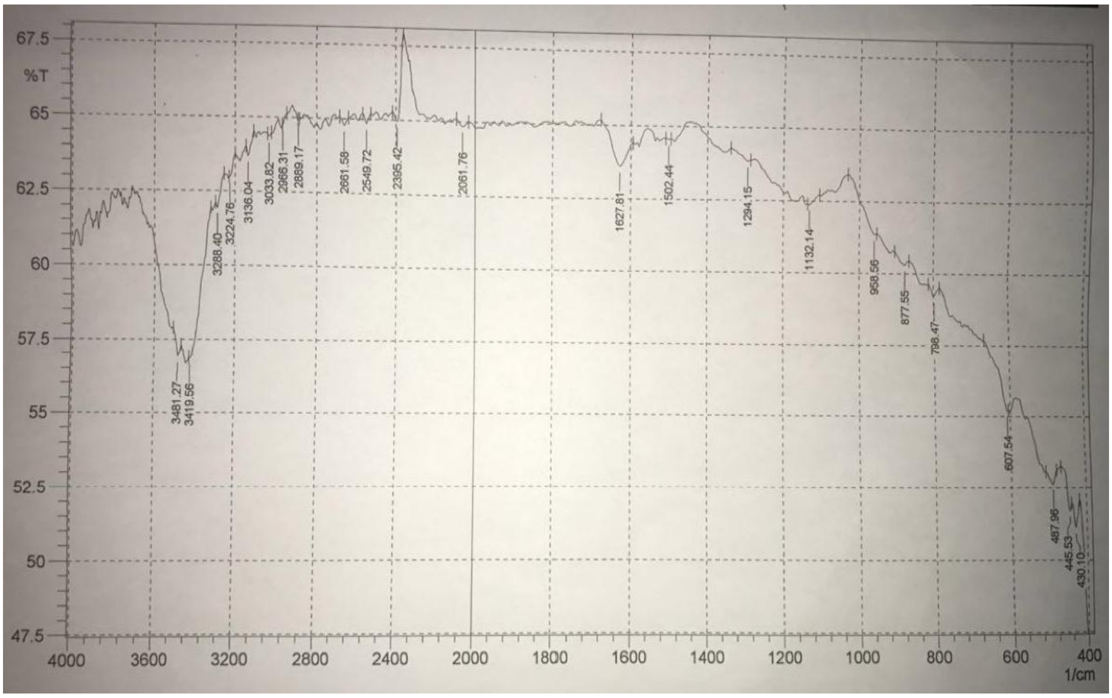
FTIR was performed on SWCNTs and MWCNTS in state of raw and modification with different processors in the range of about 500 to 4000 cm^{-1} for functional acidic processing F-SWCNTs compared with SWCNTs and F-MWCNTs raw functional acidity compared to raw MWCNT, as shows in Fig. 3.

The FTIR spectra of raw-SWCNTs show a wide peak at 3419.56 cm^{-1}, that belong to re-extends O-H to the hydroxyl group of Fig. 3 (a) that attributed to fluctuation of carboxyl group. Because of the oxidation of SWCNTs surfaces throught purification by the manufacturer can be Carboxyl groups on the outer surface of raw-SWCNTs. The frequency of carboxylation expansion at SWCNT was at 1693.38 cm^{-1}, refer to that carboxyl groups formed by the partial oxidation some of carbon atoms on SWCNTS by HNO3 and H2SO4. The band (O- H) stretching at 3417.63 and 1716.53 cm^{-1} in the MWCNT-COOH spectrum, and can be allocated to OH extension of carboxylic groups (O =C-OH and C–OH), whereas, the peak at (1703 $cm^{-1)}$ Not identical. The peak can be tied to 1118.64 cm^{-1} with the spinal cord of carbon nanotubes [16]. The signal at 1163 cm^{-1} may be related to the expansion of C-O in the same functions while the peak at 1734 cm^{-1} is associated with acid functionalized F-SWCNT with O–H Deformation of the acid group of carboxylic. the broad absorption level is due to 3417.63 cm^{-1} cause to O-H expansion of the hydroxyl groups, that can be traced to oscillation of carboxyl groups (O = C–OH and C–OH) [7].

Acid treatment of MWCNTs as compared with raw-MWCNT is shown in Fig .3. From the results, it can be observed typical bands corresponding to carboxyl groups (COOH) and hydroxyl groups (–OH) generated on the modifying MWCNT surface. In Fig.3 (b), a peak at 1118.64 cm^{-1} is related to the fact that double stretching bound C=C of the MWCNTs. For acid treatment, broad absorption band has been seen at 3417.63 cm^{-1} and 3738 cm^{-1} which is impute to O–H extent of the hydroxyl group. Those bands related to the oscillation of hydroxyl groups –OH, The carboxylic groups of F–MWCNTS were confirmed by (FTIR) at 1734 cm^{-1} (C=O) AS shows in Fig.3(b) Because of the oxidation of the surfaces for (MWCNTS) during treatment with a mixture of acids, carboxylic groups can be on F-MWCNTs surfaces. There is some peaks appear around 1627.81 cm^{-1} that resulted from the mono-boundary origin (C-C) indicate the presence of MWCNTs.

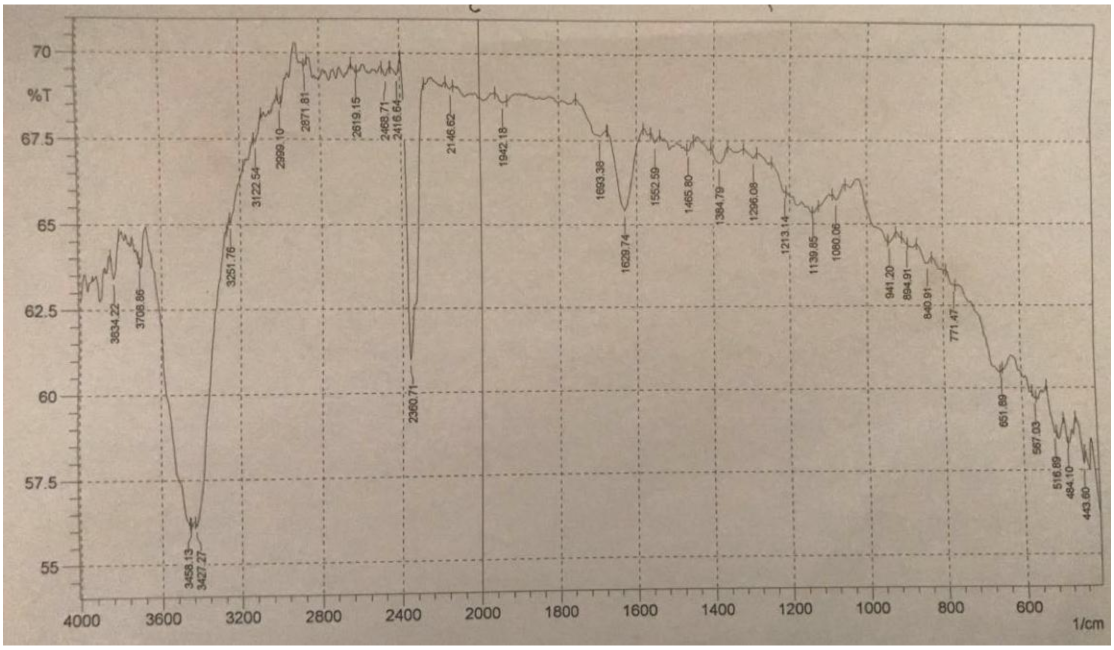


(a) Raw MWCNT

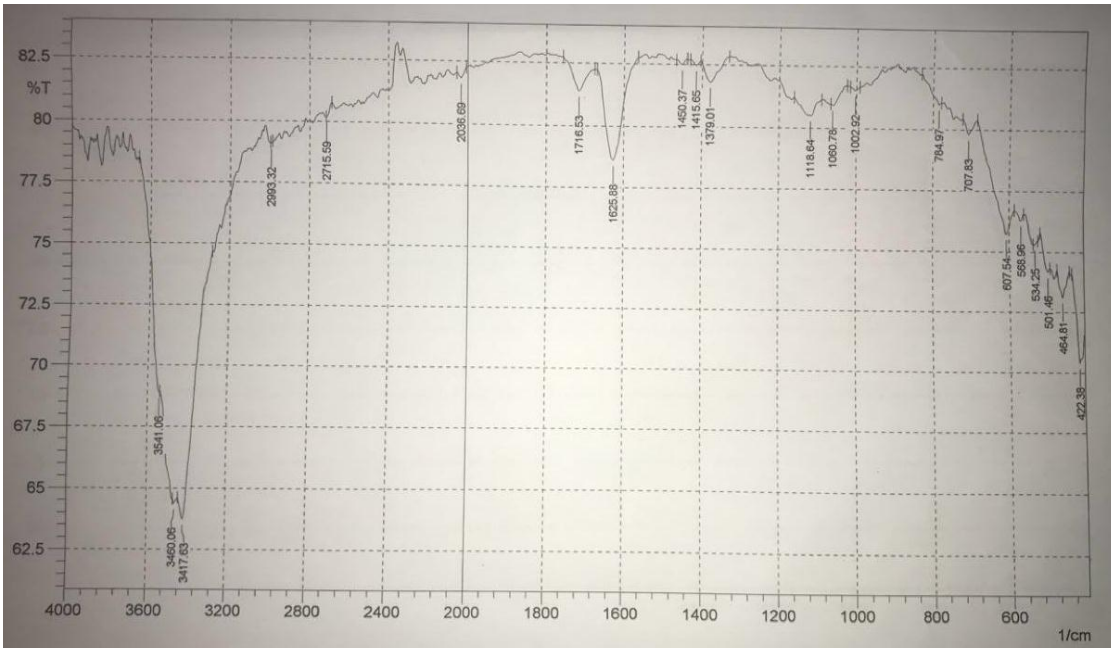


(b)Raw SWCNT

Fig.3: (a) Raw-MWCNTs and (b) raw-SWCNTs FTIR spectra.



(c) Functionalized SWCNTs

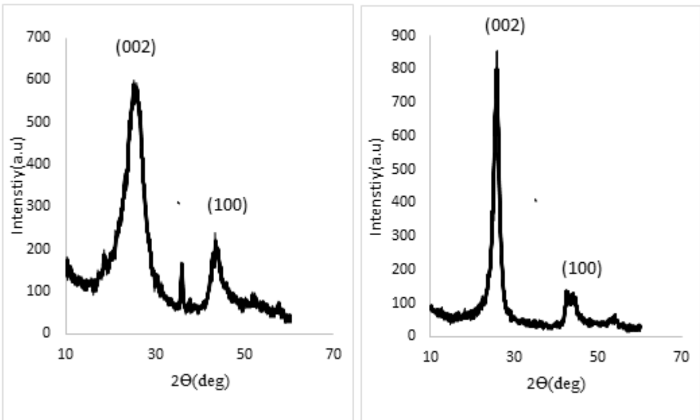


(d) Functionalized MWCNTs

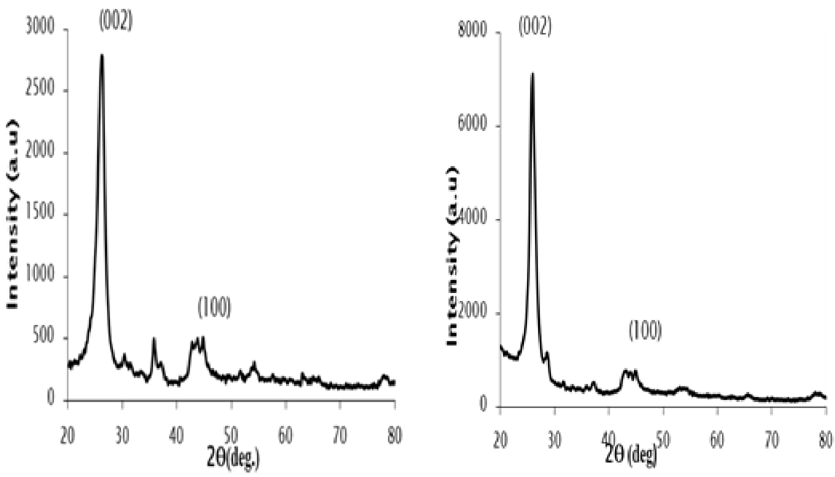
Fig.3: (c) Functionalized SWCNTs by nitric acid and sulfuric acid treatments and (d) functionalized MWCNTs by in nitric acid and sulfuric acid treatments.

X–ray diffraction patterns

X-ray diffraction patterns of raw and functionalized SWCNTs and MWCNTS as qualified in preceding work [11, 12]. As show in Fig. 4 is expected, where the significant diffraction pattern of raw SWCNTs appears at 2Ө of 26.1 as shown in Fig.4(a) The vertices of 2Ө peaks (002) correspond to reflection planes or are recognized as interlayer spacing among closet graphite layers, the reflection peak (002) were noticed at the same 2Ө values in as–synthesized and functional SWCNTs. Diffraction, Fig.4(a) shows the Diffraction peak intensity of SWCNTs at (002) in HNO_3 and H_2SO_4 acid treatments of that increasing to (IF - HNO 3= 284 and IF-H_2SO_4 = 252), respectively as compared to the raw-SWCNTs (Ir =204). These results reveal loose of the CNTs fibrilla after acids treated and forming more Straighten CNTs floss in functionalized SWCNTs. From XRD patterns of the functionalize SWCNTs samples, it's shown that the XRD patterns were same to the as–synthesized SWCNTs. From XRD patterns, it can be concluded that functionalized SWCNTs is still has same cylinder wall structure and inter planner spacing after the functionalization process. SWCNTs structure was protected even after undergone the treatment as confirmed from XRD analysis previously. Fig.4(b), shows the X-Ray diffraction patterns of process MWCNTS. As described in the other works, at the same 2ϴ values in as-synthesized and functionalized MWCNTs diffractions. And in Fig.4(b) the intensity of diffraction peak at (002) in nitric acid and sulfuric acid of the carbon nanotubes floss after process of treatment and form more arrange CNTs Floss in the functionalized MWCNTs treatments of MWCNTs was increased to (IF-HNO_3=284 and IF-H_2SO_4=252), respectively, as comparable to the Raw – MWCNTs (Ir=204).



(a) raw- SWCNTs **(b) functionalization SWCNTs**



(c) raw-MWCNTs **(d) functionalized MWCNTs**

Fig.4: (a)Raw-SWCNTs, (b) functionalized SWCNTs using chemical methods, (c) raw-MWCNTs XRD patterns (d) functionalized MWCNTs using chemical methods.

Conclusions

This work Functionalized SWCNTs and MWCNTs were obtained by acid treatment of SWCNTs and MWCNTs with different reagents (acid oxidation methods and H_2O_2). After acid treated, good distributed SWCNTs and dispersion MWCNTs are obtaining because of (OH, C=O, and COOH) Groups generators on the surface of carbon nano tubes by FT–IR and XRD. The functional groups on surface wall of both SWCNTs and MWCNTS are effectively formed with hydrogen bonding with ethanol solution after 40 minutes. The method of resonance feature is the easy and simple rout to functionalize MWCNTs in treated without destroying the severe structure of both SWCNTs and MWCNTs. in addition, a stable system of functionalized F-SWCNTs and F-MWCNTS, has achieving and therefore the efficiency of this process has been verified to distinguish between SWCNTs and MWCNTs.

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