International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.12, pp 705-714, 2016

Synthesis and characterization of carbon nanotubes from Iraqi date palm seeds using chemical vapor deposition method

Bashaer J Kahdum[1], Abbas J Lafta*[2], Amir M Johdh[1]

[1]Kufa University, College of Science, Chemistry Department, Iraq
[2]University of Babylon, College of Science, Chemistry Department, Iraq, 51002.

Abstract : This work involves synthesis of carbon nanotubes (CNTs) from ambient raw Iraqi kentardate palm seeds (IKDPS) using chemical vapor deposition method (CVD). The synthesized CNTs were characterized using different analytical and instrumental methods to identify these produced CNTs. These methods including powdered X-rays diffraction(PXRD), Raman spectroscopy, scanning electron spectroscopy (SEM), transmission electron spectroscopy (TEM), energy dispersive X-rays (EDX), thermal gravimetric analysis (TGA), and UV-Vis reflectance spectroscopy. Crystal size of the synthesized CNTs was estimated using PXRD. Raman spectroscopy was used to investigate the growth of CNTs. Morphology and dimensions of CNTs were investigated using both TEM and SEM. The ratio of elemental composition of CNTs samples was investigated via using EDX.TGA was used to determine the purity and thermal behavior of the produced CNTs. Energy band gab of the produced materials was measuredusing UV-Vis reflectance spectroscopy. Functional groups of the CNTs surface were investigated using Fourier transform infrared spectroscopy(FTIR).
Keywords : Synthesis of carbon nanotubes, Iraqikentar date palm seeds, chemical vapor deposition method.

Introduction

During last few years carbon nanotubes research top have gotten much interest over the world. This importance is coming from the role of CNTs in both scientific and applied fields [1, 2]. Their spotting can be seen in electric arc discharge experiments , catalytic processes, medical and biological applications and in fullerene synthesis[3]. Carbon nanotubescan be produced by differentmethodssuch as gas solid reactions such as arc discharge, laser ablation, catalytic chemical vapor deposition (CVD), and plasma adjutant deposition [3].The quality and quantity of the produced CNTs were understanding as to adopt on the sort of the discharge methods, the circumstances annealing duration, annealing temperature, refluxingtemperature, refluxing duration, system geometry, the electric current and voltage applied, and kind of acids utilized for the reflux [4–6]. Experimental works reported that these tubes can be either with metallic [7] or semiconductorformant[8, 9]. Theoretical electronicband structure calculations have been predicted thatthe chirality (n,m) catalogues and diameter determine whether a single walled carbon nanotubes(SWCNTs) have a metallic or semiconducting properties[10,11]. Because of their distinctive properties, CNTs were appealing materials for a varied range of applications such as biosensors[12, 13], fillers [14], gas and energy storage [15], proficient source of electron field emitters [16], that enabled production of field-effect transistors based on distinct single-and multi-wall with

analyzed performance [8,17,18], chargeable batteries [19], and semiconductor tools [20]. Additionally, for their entry effect narrow diameter of single walled carbon nanotubes were required for applications in carbon nanotube- based field effect transistors [8] than larger diameter multi walled carbon nanotubes(MWCTS) in several semiconductor procedures, where band gap of semiconducting CNTs can be reduced by increasing diameter [19].Chemical vapor deposition techniques (CVD) are the simplest, inexpensive, and most flexible devices as compared with the other kinds for this purpose [21].This method generally depend on production a precipitation process at high temperature for the clouds of precursor vapor which mainly contains an favorable percentage of carbon atoms [22].

The present study describes synthesis of carbon nanotubes (CNTs) from ambient Iraqi kentar date palm seeds (IKDPS) using chemical vapor deposition methods. These synthesized CNTs were investigated using different analytical and spectroscopic methods.

Materials and Methods

Used chemical

The used chemical in the present study were nitric acid 70% (Fisher Company), hydrogen peroxide 30% (Barcelona- Spain), nitrogen gas 99.99% (Emirates industrial gases), ethanol 99.85% (J.T. Baker) and multiwall carbon nanotubes (Aldrich Company). Carbon nanotubes were synthesized using Iraq kentar date palm seeds using modified chemical vapor deposition method.

Preparation of carbon sources

In the current study, the source of carbon materials that was used to synthesize carbon nanotubes was Iraqikentar date palms seeds which was used as a raw agricultural wastes. Before using seeds in the preparation of CNTs, simple treatments were carried out to make IKDPS samples more suitable for treating in the synthesis system. The treatments include washing, drying at 100^0C for four hours, in addition thermal treatment with milling through the thermal treatment at 150^0C to remove all traces of moisture and other wastes, and to produce simple material that can be combusted in the burning reactor chamber. Fig. 1 shows image description of these processes.

Figure 1. Image of Iraqi kentar date palm seeds that were used as raw materials for CNTs synthesis

Burning reactor

The process of synthesizing CNTs firstly depends on evolution of the carbonaceous substances as a gas phase from date palm seeds which are non-volatile and must direct sources of energy or devices to produce the carbonaceous materials from the substrate. Fig. 2 shows image description of the used burning reactor. The height of the chamber is 25 cm with a 12 cm radius. The higher part of the chamber consists of two parts made from Teflon (quick fit) to avoid gases leaking out by a suitable groove 8 cm in radius. The Teflon part includes three holes, two of which are for the input and output of the carrier gas and the evolved gases from the reactor, and the third is for the input of the carbon precursor.

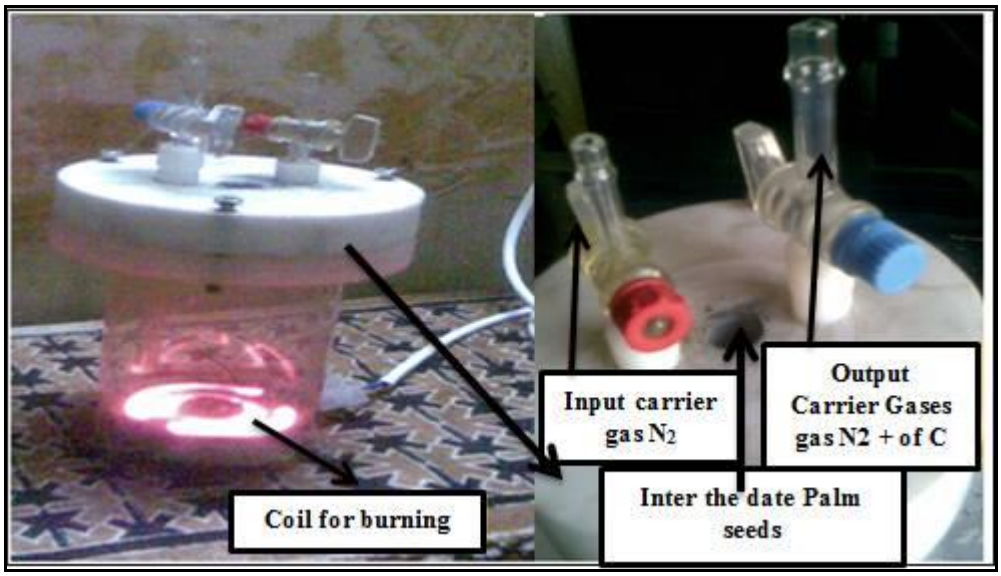

Figure 2. Image description of the used burning reactor that was used in synthesis of CNTs

Furnace of chemical vapor deposition(CVD) operation

The tube furnace that was used in this study was XIN YOO electronic components co. Ltd, block diagram of this furnace is shown in Fig. 3.The first step in this section was processed by inserting ceramic boats as a supporter andit was locatedat center of the tube furnace, which is the optimum position of heat regain for precipitation. The prepared seed samples were placed in the combustion chamber with a complete linkage to the rest of the reactor. Before switching on the furnace, nitrogen gas was purged to complete the removal of the air from the all the reaction chamber systems. The furnace was then switched on and heated to the reaction temperature. Synthesis was conducted at 750 °C under atmospheric pressure, with a typical reaction time of 30 minute in nitrogen atmosphere and arate flow of 100 cm^3/min. When the furnace attained the desired temperature the N_2 gas flow was reduced slowly to a rate of 50 cm^3/min. Then waste date palm sample was added to the reaction by switching on the combustion heater and running in the form of batches. After depositionthe furnace was switched off and allowed to cool down to room temperature under a continuous N_2 flow, then the product was collected for purification before the characterization processes.Purification processes of the producedCNTsincluded two steps: the first was heating the product in an oven for 4hours[23] and the second step was oxidation of the remaining product by (30%) H_2O_2 at 50˚C for 4 days[24].

Figure 3.Image of tube furnace that was used in synthesis of CNTs from IKDPS

Characterization of the synthesized CNTs from IKDPS

Raman spectroscopy

Raman spectroscopy was used in order to investigate hybridization of CNTs surface and to follow CNTs growth.Raman spectrophotometer used in this study was Raman spectrophotometer (Princeton Instruments).

Scanning electron microscopy(SEM)

Morphological study of CNTs surface was performed using scanning electron microscopy, SEM (Scanning Electron Microscope Inspect 550, Netherland).

Transmission electron microscopy(TEM)

High-resolution transmission electron microscopy gives a more accurate picture of the synthesized tubular structure;JEM-2100F Japan.

Powder X-Rays diffraction(PXRD)

XRD patterns for CNTs was investigated using powdered X-Rays diffraction, XRDXRD6000, Shimadzu, Japan.

Thermal gravimetric analysis(TGA)

Thermal behavior of the synthesized CNTs was investigated using thermal gravimetric analysis using ratios of the tubular structure in the synthesized sample can be found by using a TGA analysis,Netzsch, STA 449C Jupiter**.**

Fourier transform infrared spectroscopy(FTIR)

Functional groups in CNTs samples were investigated using FTIR spectroscopy. FTIR spectra were recorded with Perkin Elminer Spectrophotometer. All Samples were prepared for san by grounding with KBr crystal and mixed CNTs samples to form uniform pellets using Perkin Elmer hydrolytic pump**.**FTIR / Fourier – Transform FTIR-8400S Shimadzu, Japan.

UV-Vis reflectance spectroscopy

Energy bandgap for the synthesized CNTs was investigated using UV-Vis reflectance spectrophotometer, UV-Vis spectrophotometer-26000 Shimadzu.

Results and Discussion

Raman spectroscopy

Raman spectroscopy was used to identification of CNTs and provide important information about CNTs such as microscopic structure, electron quantum confinement,phonon and quality of tube [19]. Raman spectra are shown in Fig.4, shows three major peaks: D band at ~1364 cm^{-1} which correspondingto amorphous carbon impurities and defects in the CNTs sample, the second peak G band was shifted at ~1616 cm^{-1} because of high frequency in plan stretching of the C–C bonds, the last peak G′ band at ~2962 cm^{-1} is related to the process of double resonance [25].

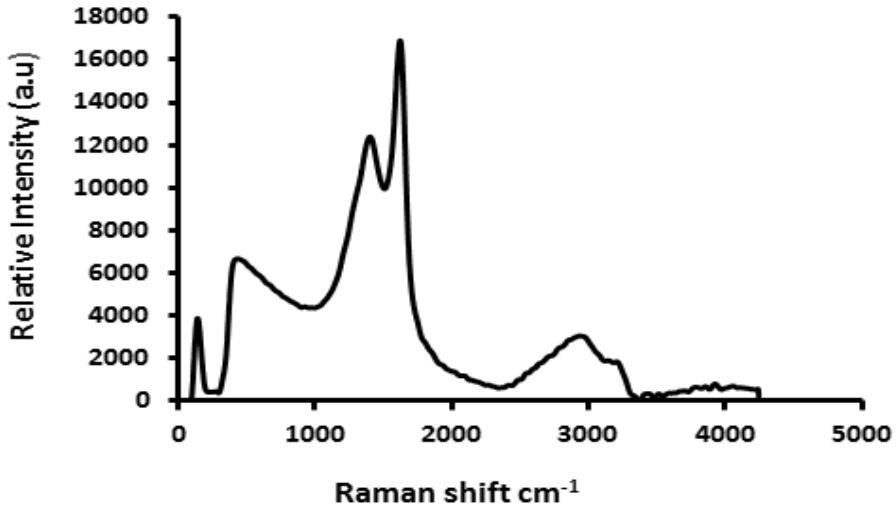

Figure 4. Raman spectra of the synthesized CNTs from IKDPS

Scanning electron microscope (SEM)

Fig. 5 shows scanning electron microscope imagesof theCNTs that were synthesized from the thermal decomposition of waste Iraqi date palms seeds. From these images the average length of the synthesized CNTS was (2-2.5)µm in length. Also, from these image itcan be seen that theaverage diameter of CNTs was around 166-200 nm, this value can be assigned to multiwall carbon nanotubes (MWNTs)[26].

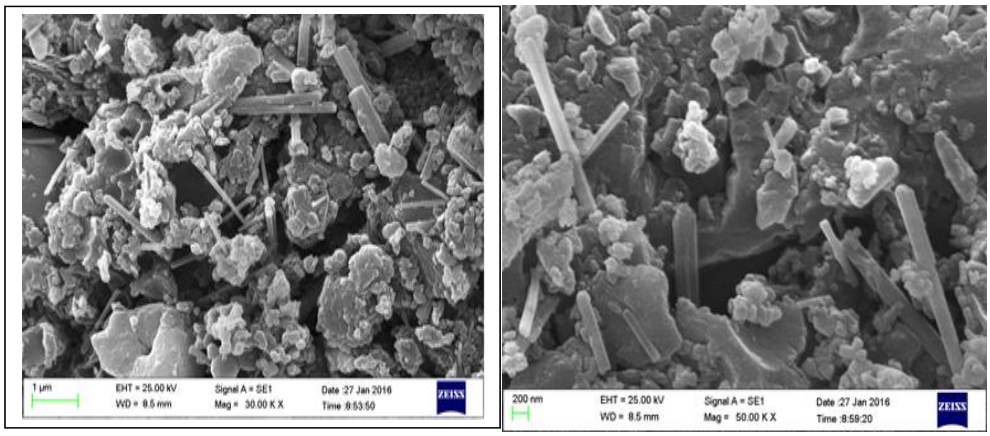

Figure 5. SEM images for the synthesized CNTs from IKDPS

Transmission electron microscope (TEM)

Images of transmission electron microscope (TEM) for the synthesized CNTs are shown in Fig. 6. These images also confirm formation of MWNTs in this procedure. The length for tubular structure was (0.6-1.5) Mm. The diameter of nanotubes was arranged between (75 – 100) nm[27].

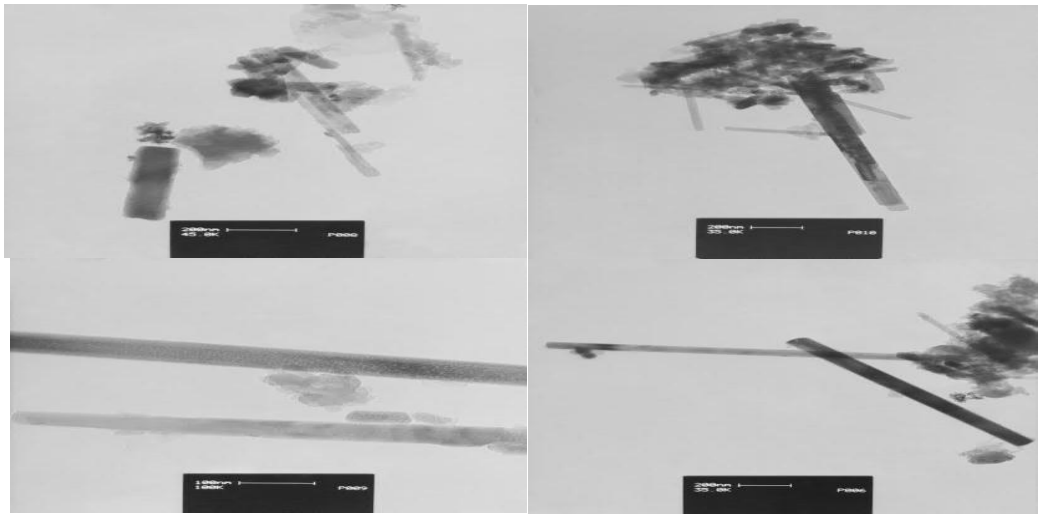

Figure 6. TEM images of synthesized CNTs grown by CVD methods at 750 ^{0}C

Energy dispersive -rays (EDX)

Elemental composition of the synthesized CNTs was investigated using energy dispersive x-ray (EDX) as shown in Fig.7. This figure shows the EDX spectra of the CNTs samples which detect the presence of C, O, Ca, and S . The peak of carbon is related to the deposited of CNTs, oxygen can be attributed to the oxygen that may be related to purification processes using hydrogen peroxide. The other elements can be attributed to the instruments. ESX results also showratios of quantitative analysis for the contents of these elements in the synthesized CNTs, which were as follows 63.22% C, 34.04% O, 1.43%S ,1.34% Ca.

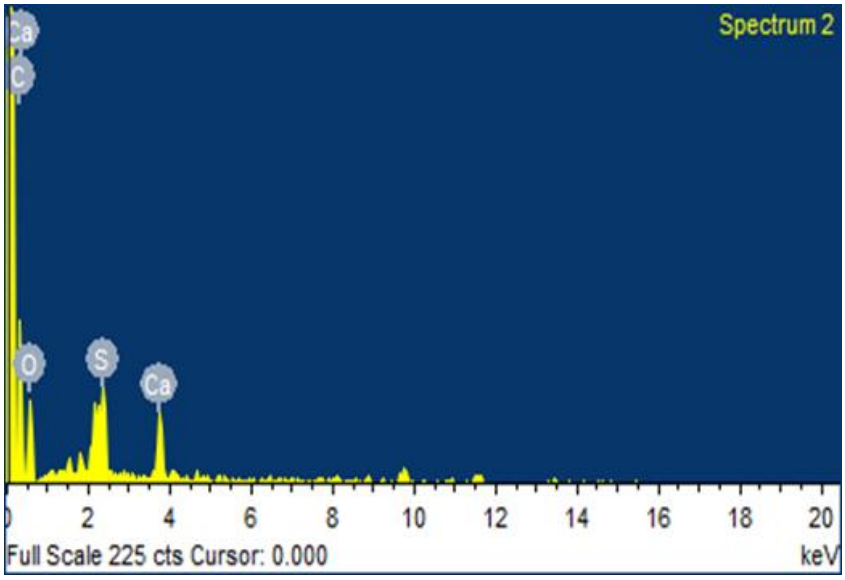

Figure 7. EDX for Synthesized CNTs from IKDPS

X-rays diffraction (XRD)

XRD measurements were carried out to examine crystal structure of synthesized CNTs.Fig. 8 shows XRD patterns of the synthesized CNTs,the peak at25.62° represents the characteristic graphitic peak arising due to the presence of the tubular structure of the carbon atoms in the sample with (002) planes.The peaks near 43.06° and 53.98^{0} are attributed to the (101) and (004) planes of the nanotubes structure, respectively [28-29].

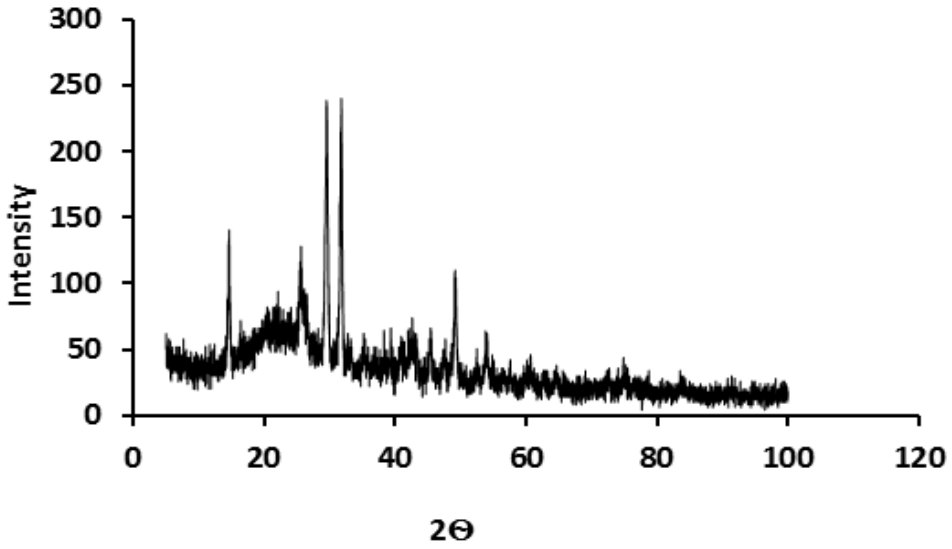

Figure 8.XRD patterns for synthesized CNTsderived from IKDPS

Thermal gravimetric analysis (TGA)

The thermal profile of CNT is shown in Fig.9. This sample shows At the temperature range of100 °C to about 170 °C, there is a mass loss of approximately 5% that can be attributed to the evaporation of the adsorbed water [30,31]. The result refers to a small weight loss from 200-300 °C, which was due to theinert of water, equals to 10% of the total weight. The gradual weight loss from 320-520 °C can be attributed to the decomposition of amorphous carbon materials. This constituted about 20% of the total weight. The dominant weight loss of 60% was due to the decomposition of the CNTs in the temperature range of 530-690°C and other non-volatile constituents made up the remaining 5% of the total weight in the temperature range of 720-800°C.

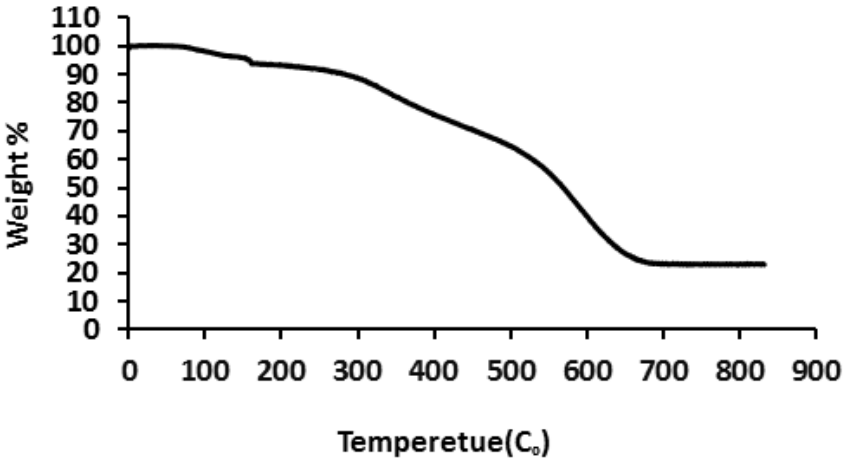

Figure 9. Schematic diagram of TGA graph for the synthesized CNTs.

UV-Visible reflectance spectroscopy

Fig. 10 shows spectrum of bandgap energy for the synthesized CNTs using UV-Visible reflectance spectroscopy. From this spectrum the bandgap energy for CNTs was equal to 3.26 eV. This value of energy fill in the range of semiconductor bandgap energy. This confirms that our synthesized CNTs fill in the range of semiconductor from energy view (2- 4 eV). The last observation is very interesting promising point which make

these materials to be as a good candidate semiconductor photocatalyst that can be used with wide spectrum of photocatalytic processes.

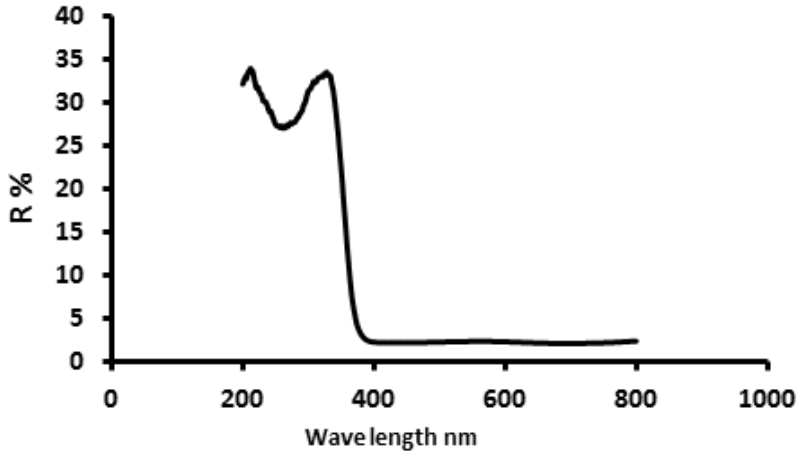

Figure 10.UV- visible reflectance spectrum for synthesized CNTs

Fourier Transform infrared Spectroscopy (FTIR)

FTIR spectra of the synthesized CNTs that were derived from IKDPs are shown in Fig.11. The peaks in the range of 699- 850 cm^{-1} are related to the characteristic peaks of graphite. The peak around 1000- 1200 cm^{-1} is related to the aromatic systems at the CNTs surface which results from destruction of the long range π system[31]. The peaks in the range 1300-1500 cm^{-1} are related to O-H groups of adsorbed water or it can be assigned to covalently bonded functional groups at the surface of CNTs[33]. The bands in the range of 1500-1600 and 1600-1700 cm^{-1} are assigned to the stretching vibrations of carboxyl and carbonyl groups [32]. The bands in the range of 400-600 cm^{-1} are assigned to the D band of CNTs [33]. The bands in the range of 2000- 2800 cm^{-1} are related to stretching vibration modes of C-H and C-H2 groups[32]. The broad band in the range of 3200-3600 cm^{-1} is related to the vibration modes of hydroxyl groups. The bands in the range of 290-3100 cm^{-1} are related to the alicyclic groups. The weak bands around 1800 cm^{-1} are elated to the presence of additional sp^3hybridized carbon atoms[32].

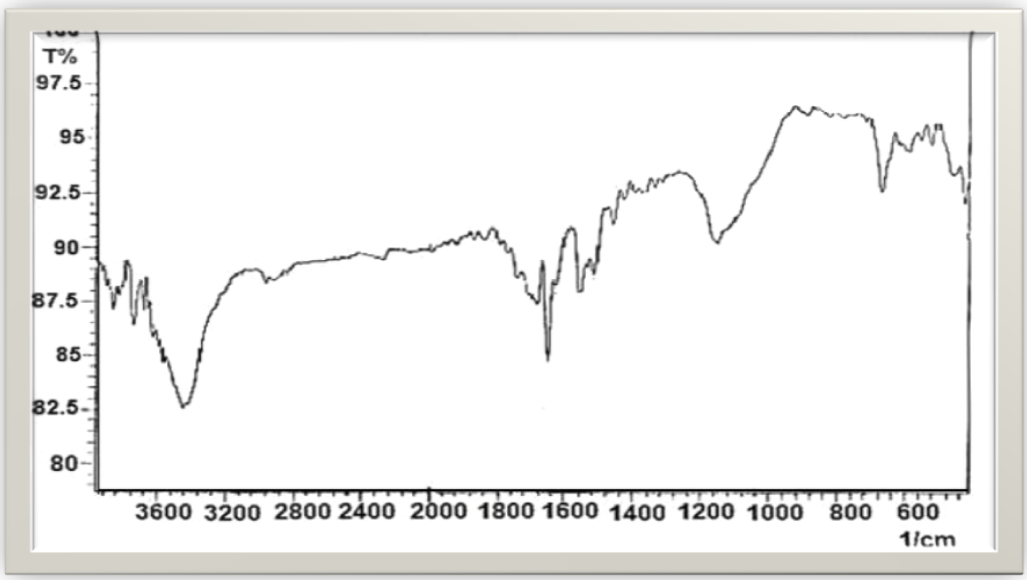

Figure 11. FTIR spectra for the synthesized CNTs from IKDPS

Conclusions

In this study CNTs were synthesized effectively from ambient agricultural raw material which was Iraqi kentar date palm seeds. These synthesized CNTs were characterized using different analytical and spectrophotometric methods.

References

1. C. Manoharan C. , R. SakthiMurugan R. &Dhanalakshmi A.(2016).Preparation of Magnetite (Fe_3O_4) Thin Films by Sol- Gel Method and its Characterization. International Journal of ChemTechResearch, 9(6), 401-407.
2. Suriyavathana. M, & Ramalingam.K., (2015). Nanoparticles Synthesis and Antibacterial Study on AnisomelesMalabarica using Manganese Oxide (MnO). International Journal of ChemTech Research , 8(11), 467-473.
3. PrachiP.,Gautam P., Deepa M.,&Brijesh N. (2013). Nanotechnology in Waste Water Treatment: A Review. International Journal of ChemTechResearch.5(5), 2303-2308.
4. Yoshinori A., Xinluo Z., Sakae I &Iijimaa S. (2002). Mass production of multiwalled carbon nanotubes by hydrogen arc discharge. Journal of Crystal Growth.,237(1), 1926-1930.
5. Shi Z., Lian Y., Zhou X., Gu Z., Zhang Y., Iijima S., Zhou L.,Yue T.&Zhang S.(1999). Mass production of single-wall carbon nanotube by arc discharge method.Carbon.37(9), 1449-1453.
6. Stancu M., Ruxanda G., Ciuparu D&Dinescu A. (2011). Purification of multiwall carbon nanotubes obtained by AC arc discharge method. Optoelectronics and Advanced Materials. 5 (8), 846-850.
7. Tans S., Devoret M., Dai H., Thess A., Smalley R., Georliga L.& Dekker C.(1997). Individual single-wall carbon nanotubes as quantum wires.Nature.386,474-477.
8. Tans S., Verschueren R.& Dekker C.(1998). Room temperature transistor based on a single carbon nanotube.Nature. 393,49-52.
9. Burke P., Rutherglen C. & Yu Z. (2006). Single-Walled carbon Nanotube: applications in high frequency electronics.International Journal of High Speed Electronics and Systems. 16(4), 977-999.
10. Hamada N., Sawada S. &Oshiyama A.(1992).New One-Dimensional conductors: Graphitic Microtubules.Phys.Rev. Let.68,1579-1581.
11. Garau C., Frontera A., Quinonero D., Costa A., Ballester P.&Dey P. (2003). Lithium diffusion in single-wall carbon nanotubes:a theoretical study. Chemical Physics Letters.374(5-6), 548-555.
12. Dai H.,.Hafner J., Rinzler A., Colbert D.&Smalley R.(1996). Nanotubes as Nanoprobes in Scanning probe Microscopy.Nature.384,147 150.
13. Lau K., ChongG.&Hui, D.(2006). A Critical Review on Nanotube and Nanotube/nanoclayRelated Polymer Composite Materials,Compos Part B: Eng.37(6), 425-436.
14. Ahn J., Wang G.,. Liu H. &Dou S.(2003). Nanoparticle-dispersed PEO polymer electrolytes for Li batteries.Journal of Power Sources.119-121,422-426.
15. De Heer W., Chatelain A.&Ugarte D. (1995). A Carbon Nanotube Field-Emission Electron source.Science.270(5239), 1179-1180.
16. Martel R., Schmidt T., Shea H., Hertel T.&Avouris P.(1998).Single- and multi-wall carbon nanotube field-effect transistors.Applied PhysicsLetters.73,2447-2449.
17. Alexander A., Lee S., Mei Z., Baughman R. &Zakhidoy A. A.(2010). Electron field emission from transparent multiwalled carbon nanotube sheets for inverted field emission displays.Carbon.48(1),41-46.
18. Kun F., Yildiz O. , Bhanushali H., Wang Y., Stano K., Xue L.,Zhang X. &Bradford P.(2013).Aligned Carbon Nanotube-Silicon sheets: A NovelNano-architecture for Flexible Lithium IonBattery Electrodes.Advanced Materials..25(36), 5109- 5114.
19. Jensen A., Hauptmann J., Nygrd J., Sadowski J. &Lindelof P.(2004). Hybrid Devices from Single Wall Carbon Nanotubes Epitaxially Grown into a Semiconductors Heterostructure. Nano Letters.4(2),349-352.
20. Gnanasangeetha D., &SaralaThambavani D., (2015). Green Zinc Oxide Nanoparticle Ingrained on Activated Silica for the Removal of As(III) from aqueous solution using Ocimum sanctum and Azadirachtaindica. International Journal of ChemTech Research, 8(8), 44-52.

21. Jan P., Jana D., Jana C., Jaromir H., Ondrej J.,Vojtech A. &Rene K. (2011).Methods for carbon nanotubes synthesis – a review.Journal of Materials Chemistry.21, 15872-15884.
22. Lubej M.&Plazl I. (2011). Theoretical descriptions of carbon nanotubes synthesis in a chemical vapor deposition reactor : a review.Chemical and Biochemical Engineering.26(3), 277-284.
23. G. Che, B. Lakshmi, C. Martin, E. Fisher.(1998). Chemical Vapor Deposition Based Synthesis of Carbon Nanotubes and Nanofibers Using a Template Method.*Chem. Mater*.10, 260-267.
24. Shaijumon M. &Ramaprabhu S.(2003). Synthesis of carbon nanotubes by pyrolysis of acetylene using alloy hydride materials as catalysts and their hydrogen adsorption studies.Chemical Physics Letters. 374(5-6), 513-520.
25. Mildred S., Ado J., Mario H., Gene D. &Riichiro S.(2010).Perspectives on carbon nanotubes and graphene Raman spectroscopy. Nano Letters. 10(3), 751-758, 2010.
26. Elsa G., Manuel R., Alfredo A.& Francisco E.(2013).Synthesis of Carbon nanotubes of few walls using aliphatic alcohols as a carbon source.Materials.6(6), 2534-2542.
27. Szbo A.,Perri C., Csato A. ,Giordan G.,Vuono D. &Nagy J.(2010). Review:synthesis methods of carbon nanotubes and related materials.Materials.3(5),3092-3140.
28. Nishimura K., Okazaki N.,Pan L.&Nakayama Y.(2004). In Situ Study of Iron Catalysts for Carbon Nanotube Growth Using X-Ray Diffraction Analysis.Japanese Journal of Applied Physics, 43(4A), 471–474, 2004.
29. Capula S., Aguir K., Cervantes F., Villa L., Moncayo J. &Vicente G. Febles G.(2014).Ozone Sensing Based on Palladium Decorated Carbon Nanotubes'', Sensors.14(4), 6806-6818.
30. Datsyuk V.,Kalyva M.,Papagelies K.,Parthenios J. ,Tasis D.,Siokou A., Kallitsisa I.&.Galiotis C.(2008). Chemical oxidation of multiwalled carbon nanotubes.Carbon.46(6),833-840.
31. Hussain S., Jha P., Chouksey A., Raman R., Islam S., Islam T.,.Choudhary P. &Harsh.(2011). Spectroscopic Investigation of modified Single wall carbon nanotube (SWCNT).Journal of Modern Physics.2, 538-543.
32. Kuhlmann U., Jantoljak H., Pfander N., Bernier P., Journet C. &Thomsen C.(1999). Infrared reflectance of single-walled carbon nanotubes.Synthetic Metals.103(1-3), 2506-2507.
33. Branca C., Frusteri F., Magazu`V.&Mangione A. (2004).Characterization of Carbon Nanotubes by TEM and Infrared Spectroscopy.Journal of Physical Chemistry B. 108(11), 3469-3473.

*****