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Synthesis of Carbon Nanotubes with A Few Walls by Chemical Vapour Deposition Method Using A Mixture of Ethanol/N-Propanol As A Source of Carbon Species

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Abstract

The current study explains synthesis of carbon nanotubes (CNTs) with a few walls (FWCNTs) using a mixture of equal ratios of aliphatic alcohols (1:1) ethanol/propanol by applying chemical vapour deposition method(CVD). This method was conducted using a tube burner reactor at 750 °C, *and* the synthesis was conductedon a silica surface. FWCNTs, as product, was characterized using Scanning electron microscopy (SEM), X-rays diffraction (XRD), Energy dispersion X-rays (EDX), Raman spectroscopy, Thermo gravimetric analysis(TGA) and Fourier-transform infrared spectroscopy (FTIR). The sizes of FWCNTs ranged of (40-60) nm, were obtained, with lengths about 6 µm. The majority of CNTs have onion-like shape.
Keywords:Ethanol, Propanol, CVD, carbon nanotubes (CNT).

1. Introduction

Carbon nanostructures are the most significant nanoscale materials, referring to structures composed of carbon molecules that are connected to each other with a sp^2 hybridization with graphene or graphite as a layer. It's similar to the pattern of honeycomb or a network of hexagons made up of carbon atoms. Carbon nanotubes are divided into two moieties based on the sequence in which their graphene sheets are wrapped up into cylinders: single-walled carbon nanotubes(SWCNTs) and multi-walled carbon nanotubes(MWCNTs). Carbon nanostructured with a single wall can be existed as a metal or a semiconductor. This depends on contingent of the direction of wrapping helicity and the diameter of the produced tube [1].

The second form of carbon nanotube is multi-walled carbon nanotubes, which differs from SWCNTs in that they are made up of more than two layers of graphene species that are folded into a cylinder. Carbon nanomaterial with a few walls are a comparatively recent class of CNTs (FWCNTs) [2], that are a type of MWCNTs that has architectural completeness comparable with SWCNTs and consists of (2-6) graphene layers. This new type of CNTs falls between SWCNTs and MWCNTs. This type typically has a diameter ranging from 0.5 to 100 nm, and their length might be measured in millimeters. SWCNTs have a diameter of approximately 1 nm and a length of less than 20 cm, whereas FWCNTs have a diameter around 4-7 nm [4-5] and cross CNTs (MWCNTs) have a diameter around 10 nm [3]. In general, carbon nanotubes have unique optical, magnetic, electrical, chemical, and physical properties due to the nature of their structure. CNTs are among the strongest fibers known to date, this phenomenon is related to their C–C bonds. CNTs are also extremely thermally stable, both in a vacuum and in the atmosphere. In this context, CNTs can be synthesized using a variety of processes, each of them differs in efficiency, cost, and quality.

Important example of these methods are laser ablation, chemical vapour deposition method, sol-gel method and Arc discharge method [6-8]. The outcome of these processes is huge in amount and contains additional byproducts, such as amorphous

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carbons and catalyst, which must be extensively purified before high quality carbon nanotubes can be obtained. Among different methods that can be utilized in synthesizing of CNTs, CVD seems to be a typical way to synthesize pyrolysis of hydrocarbons over a catalytic powder creating carbon nanomaterial's; without a catalyst, carbon clouds deposit in the formation of nanotubes happens on a particular spot [9]. The highly reactive carbon sources used in low-temperature CVD synthesis are methane [10], ethylene[11], acetylene[12], benzene[13], carbon monoxide [6,7,14], and cyclohexane [15]. Alcohols are a viable alternative carbon source that can be used in synthesizing of CNTs, despite being less reactive, this observation is due to producing of high-quality CNTs upon using these materials as carbon source[16]. This benefit comes from the hydroxyl radical etching of the produced amorphous carbon, which extends the catalyst's lifespan and produces higher-quality CNTs. The hydroxyl radicals are produced by either alcohol thermolysis or the addition of water vapour as an auxiliary additive [17].

The forms and skeletons of carbon nanotubes generated using this approach are influenced by the molecule of the precursor, ethane, ethylene, and acetylene are linear hydrocarbons that thermally breakdown into atom carbon or linear dimmers and trimmers of carbon, resulting in hollow CNTs. Branching CNTs are produced by predecessors with even more than seven carbon atoms, whereas cyclic compounds like xylene, benzene and cyclohexane yield curved CNTs with curving tube walls, numerous of which are linked. CVD was employed in this study to make CNTs from alcohols for example 1-propanol, ethanol and 2-propanol. Atmosphere pressure and 750°C are used in this technique[17].

The present work would involve synthesis of CNTs using a chemical vapor deposition method. In this approach a mixture of (1:1) of ethanol and propanol would be used as a source of carbon. The proposed synthesized CNTs would be investigated using different spectroscopic and analytical techniques.

2. Experimental

*2.1. **Materials***

Ethanol (99.99%) was supplied by J.T. Baker,1-propanol (99.99%) was provided by sigma Aldrich. Hydrogen peroxide (30%) was supplied from Barcelona, Spain. Nitrogen gas N_2 with a purity of 99.99 was supplied by Emirates industrial gases.

*2.2. **Methods***

2.2.1. Synthesis of MWCNTs

Nabertherm USA technique was utilized in synthesizing of carbon nanotubes using chemical vapour deposition method CVD. This process was performed in a tube furnace with three steps. This furnace has two quartz tubes: inner one with a length of 125 cm and a diameter of 4 cm, and the outer one with a diameter of 6 cm and a length of 110 cm.

The ceramic boat was placed in the tube furnace's optimal precipitation area, which is placed in the center of the inner tube. To eliminate the air from the reaction chamber systems before turning on the tube furnace, N_2 gas was flushed as a carrier at a 100 cm^3/min flow rate. For 35 minutes prior to starting synthesis processes. Then, the furnace was heated to reach 550 ^oC under atmospheric pressure. Then, N_2 gas flow was progressively lowered to 80 cm^3/min after the furnace achieved the desired temperature. After passing N_2 gas through a vaporizer containing a 1:1 methanol/propanol mixture (١٥٠ mL) that was evaporated at 80 ^oC. In this manner N_2 gas held a vapor of alcoholic mixture, which isa carbon source. After the deposition was completed, the furnace was turned off and allowed to cool to ambient temperature while nitrogen gas was still flowing at rate 80 cm^3/ min. The produced CNTs was collected from furnace in order to be processed properly. The apparatus of the unit that is utilized in synthesis of CNTs is shown in Figure 1.

The purification of the synthesized CNTs was performed by immersing the product in 200 mL of ethanol for 20 minutes using an ultrasonic water bath. Using a separating funnel, re-distributed the collected particles. At 20 ^oC for 14 hours, the bottom partial was detached and dispersed with 100 mL of H_2O_2, 100 mL of deionized distilled water was added to dilute the solution. The mixture was progressively heated to a temperature of 50 ^oC for 30 minutes to finish the dissolving of the residual H_2O_2. The obtained CNTs was washed many times with DI-distilled water before being dried at 100 °C for 15 hours.

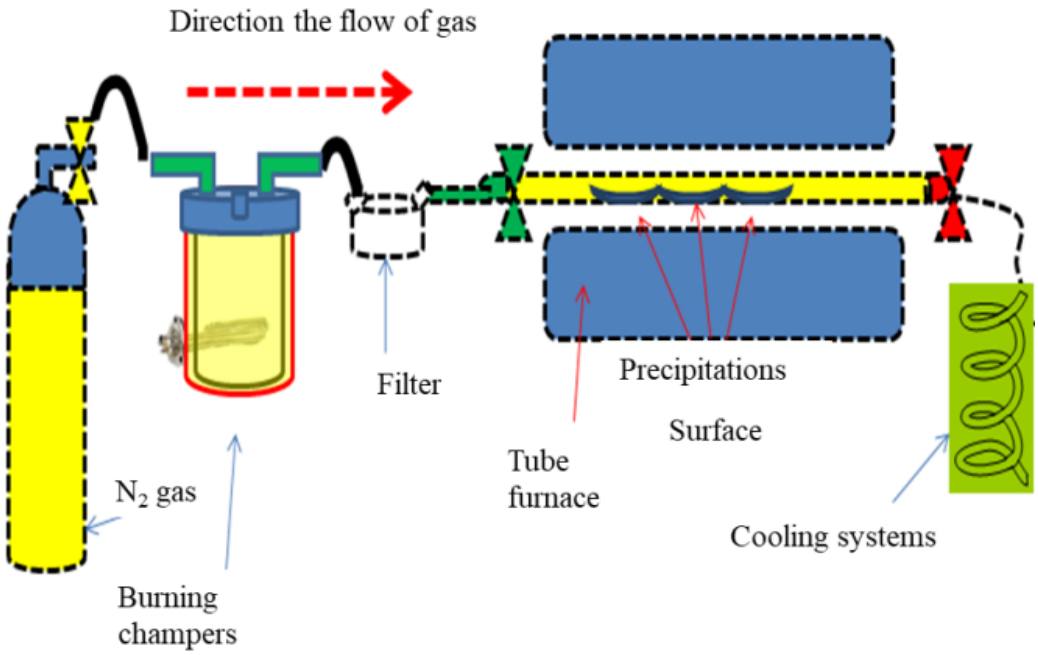

Fig. 1. Schematic description for the unit that was used in synthesis of CNTs according to CVD approach.

2.2.2. Characterization of the synthesized CNTs

The produced CNTs was investigated using different spectroscopic and analytical techniques. X-rays diffraction (XRD) using a Cu K radiation wavelength 0.15405 nm and a (XRD6000, Shimadzu, Japan) X-ray diffractometer. A tube with a voltage of 40 kV and a current of 100 mA was used. Raman spectra was performed using Sentara Infinity Bruker, JEOL AR and EDX Broker X-Flash 5030 detectors were used to create SEM pictures. Thermalgravimetric analysis was performed using (STA.PT.1000, LINSEIS Germany). The TGA studies were carried out by burning from a comfortable 25 °C to 900 °C at a rate of 10°C/min in dry air flow at a rate of 50 ml/min. Fourier – Transform Infrared spectroscopy using FTIR spectrophotometer - 8400S, Shimadzu, Japan, using KBr disc in a ratio of (1/50) measurements were conducted in the range from 200-4000 cm^{-1}.

3. Results and discussion

*3.1. **Raman shift spectrum***

Raman spectra for the synthesized CNTs using a mixture of ethanol/propanol (1:1) as a source of carbon are shown in Figure 2. These spectra show two main peaks of the major characteristic graphite bands. The band around 1400 cm^{-1} is related to D band of sp^3 amorphous carbon. The band around 1650 cm^{-1} is related to G band of crystalline sp^2 carbon. Generally, these characteristic peaks D and G appear in the range of 1250 to 1450 cm^{-1} for D band and for G band appear in the range of 1600-1700 cm^{-1}. This depends on the type of produced CNTs and presence of impurities [18]. Most carbon isotopes, particularly amorphous carbon sp^2 have the G band around 1577 cm^{-1}, the G band is related to the lateral shear stage of carbon atoms attributed to in vibrant of the C–C bond that matches to the graphite plane widening manner [19].

The intensity of the D to G band (I_D/I_G) indicates crystalline degree of the synthesized CNTs and in this study it was around 1.23 which indicates good crystalline quality, also according to this ratio it can be determined type of CNTs and it seems to be as FWCNTs. Also, from these spectra, it can be seen appearance of radial breath mode around 150 cm^{-1}, which is related with CNTs radius [20-21]. The weak peaks appear around 2400, 2800 and 2900 cm^{-1} can be assigned to D^- and G^- bands which are related to overlap of the two peaks G and D on tubular structure of the synthesized CNTs [21].

*3.2. **X-rays diffractionfor the synthesized FWCNTs***

XRD patterns for the synthesized FWCNTs are shown in Figure 3. From these patterns, the peaks at 2θ= 25.6, 26, 30 °, and 38, these are related to the typical graphitic peak coming from the appearance of

a tubular carbon atoms configuration in the sample with (002) and (100) planes. The peaks at 2θ = 43.85 (101) and 53.30 (004) plane can be assigned to the assembly of nanotubes. The peaks at 2θ = 33.45°, 35.38°, 41.65, and 48.4 are attributed to the amorphous carbon that is present with tubular structure of the synthesized CNTs [22,23].

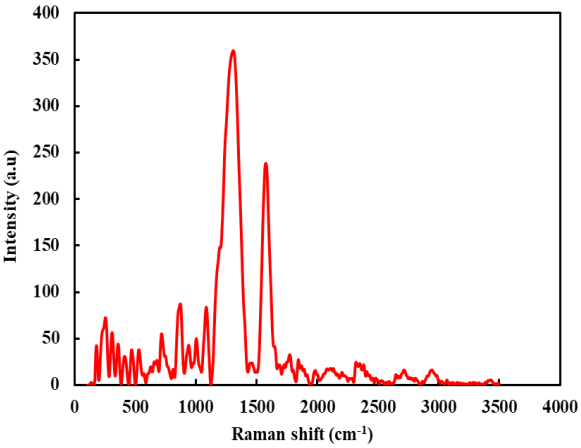

Fig. 2. Raman spectra of FWCNTs synthesized at 750 ºC using a mixture of ethanol/propanol.

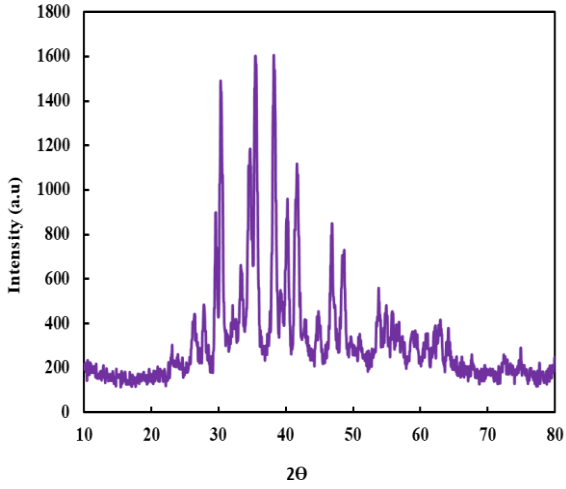

Fig. 3. XRD patterns for the FWCNTs synthesized at 750ºC using a mixture of ethanol/propanol(1:1).

3.3. Scanning electron microscopy for the synthesized CNTs

Surface morphology of the synthesized CNTs was investigated using SEM technique. The obtained images for the synthesized FWCNTs are shown in Figure 4. From these images, it can be seen formation of tubular CNTs using from alcoholic mixture as a source of carbon. Diameters of the synthesized CNTs were in the range from 40 to 60 nm and with a tublar length around 6 µm. In addition to that, majority of the material has like onion-shaped components, implying that it was made via a unique CNTs fabrication. In this manner, ethanol necessitates a considerable proclivity for edging iron nanocomposites rather than promoting the technique of forming a cylinderconfiguration, which is necessary to give lamellar constructions. Ethanol requires a greater propensity towards encircle nanopowders of iron rather than forming of cylinder configurations required to obtain lamellar structures [24-26].

The obtained results from the SEM micrographs, the average diameter for the synthesized CNTs from a mixture of ethanol/propanol(1:1) was ranged from 40-60 nm, which is greater than the one which was reported for each of ethanol and propanol alone and it was around 18 nm and 15 nm for each alcohol respectively [17], also the average length of the CNTs were around 6 µm which is greater than for CNTs that wasproduced from each alcohol alone and it was 1.2 µm and 2.0 µm respectively [17]. So it can be concluded that using a mixture of aliphatic alcohols can yield CNTs with longer length and greater external diameter in comparison with using them indivitually as a source for CNTs synthesis.

3.4. Energy dispersion X-rays for the synthesized CNTs

Elemental analysis of the synthesized CNTs was performed using EDX technique. The obtained results are shown in Figure 5. This spectrum confirms presence of C and O in the structure of the synthesized CNTs. The impurities of Si, K, Al, Ca, P, Na, Fe and Mg probably arises from activities that were conducted during purification processes for the synthesized CNTs, and other components from the instruments and sample compartments.

3.5. Thermal gravimetric analysis for the synthesized CNTs

TGA was used to examine the thermal behaviour of the CNTs that were synthesized. The TGA profile for the synthesized CNTs is shown in Figure 6. The losing weight was approximately 6% in the range of 100 to 180 ºC, can be assigned to lose of the adsorbed water [٢٧]. The evaporation of amorphous carbon causes a mass loss around 16.44 % in the range 200 – 500 °C. The weight loss in the range of 580°C to 900 °C can be related to slow oxidation steps, resulting in a loss of 30.59% of the investigated sample. The CNTs that lost between 220 and 410 °C which was around 53% of the sample's mass [28,29]..

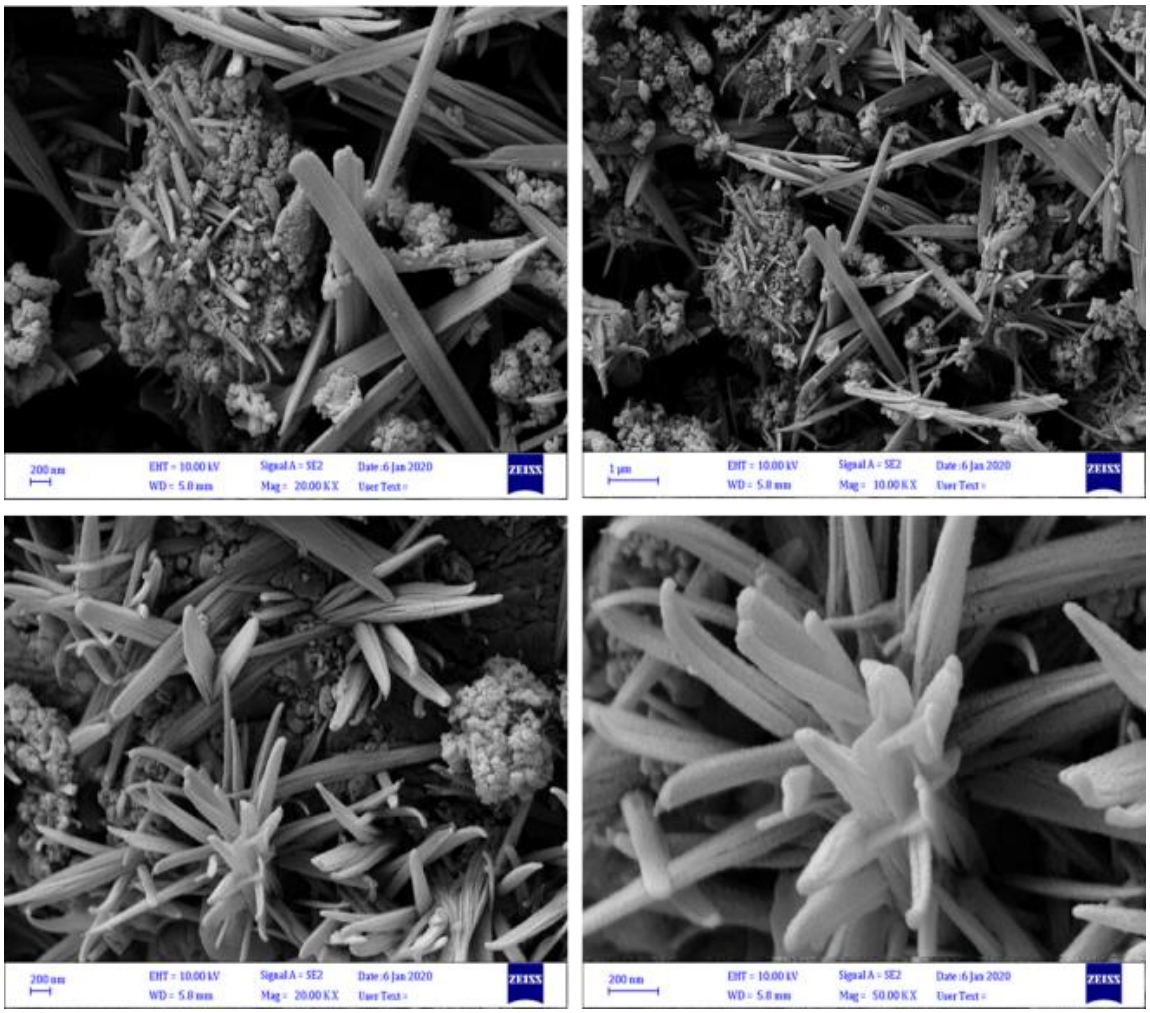

Fig. 4. SEM images of the synthesized FWCNTs at 75ºC using a mixture of ethanol/propanol (1:1).

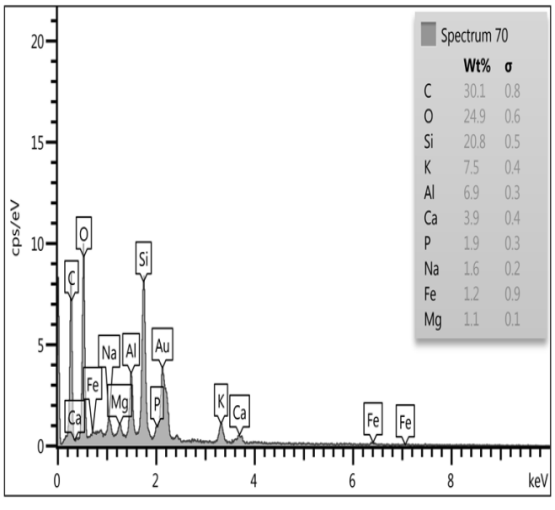

Fig.5. EDX analysis for the synthesized CNTs using a mixture of ethanol/propanol (1:1).

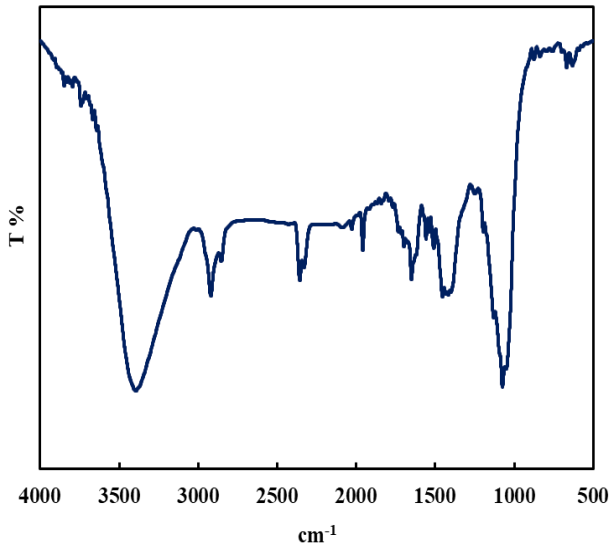

Fig. 7. FTIR spectra for synthesized FWCNTs using a mixture of (1:1) ethanol/propanol.

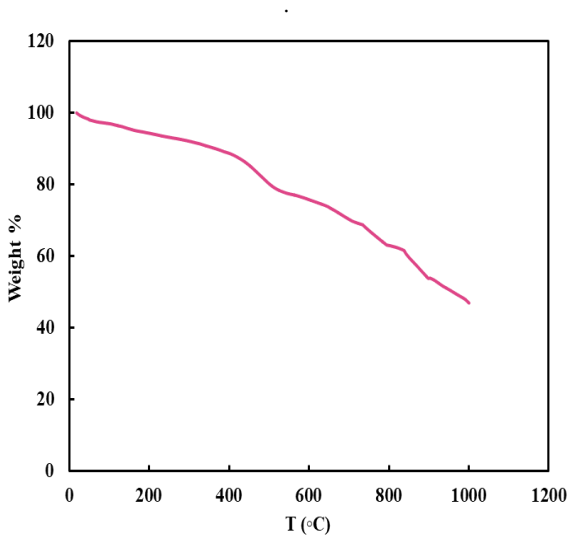

Fig. 6. TGA analysis for synthesized FWCNTs using a mixture of (1:1) ethanol/propanol.

3.6. Fourier-transform infrared spectra of the synthesized CNTs

FTIR spectroscopy was used to investigate the presence of functional groups on the surface of the synthesized CNTs. FTIR spectraof the synthesized CNTs are shown in Figure 7. From these spectra, the peak around 1690-1630cm^{-1} is assigned to the vibration of -C=C- of alkenes and that around 1500-1400 cm^{-1} can be assigned to the vibration of C-C in aromatic ring. [*27-29*]. The peak around 1760-1690 cm^{-1} can be assigned to stretching vibration modes of C=O group at the surface of synthesized CNTs, and the absorption peaks at 3500-3200 cm^{-1} is related to absorption of OH group. The peak around 1320-1000 cm^{-1}is assigned to CO stretching of CNTs. The peak around 1310-1000 cm^{-1} is assigned to stretching vibration of CO group in CNTs [30,31].

4. Conclusions

In this work MWCNTs of type only FWCNTs was synthesized successfully using a mixture of ethanol/propanol in equal ratio (1:1) of these aliphatic alcohols. Synthesis process was performed using chemical vapor deposition approach under a stream of N_2 flush at burning temperature of 750 ºC on a silica chamber. The temperature in an outer chamber that contains an alcoholic mixture was 78 ºC. This mixture has a boiling point, which is lower than that of each pure alcohol indivetually. From the obtained results, the synthesized CNTs was of type a few walled carbon nanotubes with an average external diameter around 50 nm and tube length around 6 µm. In this context, molecular contact plays a vital function in controlling the precipitation process for carbon atoms from alcohol molecules in the used mixture. Mixing has the advantage of lowering the boiling temperature, boosting mixture evaporation, and resulting in less amorphous carbon being produced.

5. Conflicts of interest

“There are no conflicts to declare”.

6. References

[1] M. García-Gutiérrez, A. Nogales, J. Hernández, D. Rueda, and T. Ezquerra, X-ray scattering applied to the analysis of carbon nanotubes, Polymers and Nanocomposite, Optical Pure Applied, 2007, **40(2)**, 195-205.

[2] A.Gruneis, M.H.Rummeli, C.Kramberger, A. Barreiro, T. Pichler, R. Pfeiffer, H. Kuzmany, T. Gemming, and B. Buchner, High quality double wall carbon nanotubes with a defined diameter distribution by chemical vapor deposition from alcohol, Carbon, 2006, **44(15)**, 3177-3182.

[3] Q.Cheng, Hang, G. Bo, C. Yuan, Q. Qi, C. Lu, Z. Otto, and L. Jie, Fabrication of Small Diameter Few-Walled Carbon Nanotubes with Enhanced Field Emission Property, Journal of Nanoscience and Nanotechnology, 2006, **6(5)**,1346-1349.

[4] D. Y. Kim, J. H. Kim, M. Li, S. Noda, J. Kim, K. S. Kim, C. M. Yang, Controllable pore structures of pure and sub-millimeter-long carbon nanotubes, Applied Surface Science, 2021, **566**, 150751.

[5] S.Y. Moon, S.Y. Jeon, S. H. Lee, A. Lee, S. M. Kim, High purity single wall carbon nanotube by oxygen-containing functional group of ferrocene-derived catalyst precursor by floating catalyst chemical vapor deposition, Nanomaterials, 2022, **12(5)**, 863.

[6] J. C. Moses, A. Gangrade, B. B. Mandal, Carbon nanotubes and their polymer nanocomposites, In Nanomaterials and Polymer Nanocomposites, 2019, 145-175.

[7]V. V. Grebenyuko, E. D. Obraztsova, A. S. Pozharov, N. R. Arutyunyan, A. A. Romeikov, I. A. Kozyrev, Arc-synthesis of single-walled

carbon nanotubes in nitrogen atmosphere, Fullerenes, Nanotubes and Carbon Nanostructures, 2008, **16(5-6)**, 330-334.

[8]N.Baig, I. Kammakakam, W. Falath, Nanomaterials: A review of synthesis methods, properties, recent progress, and challenges, Materials Advances, 2021, **2(6)**, 1821-1871.

[9]M. Kumar and Y. Ando, Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production, Journal of Nanoscience and Nanotechnology, 2010, **10(6)**, 3739-3758.

[10]M. Saeed, Y. Alshammari, S. A. Majeed, E. Al-Nasrallah, Chemical vapour deposition of graphene—Synthesis, characterisation, and applications:A review. Molecules, 2020, **25(17)**, 3856.

[11] R. Sen, A. Govindaraj, and C. Rao,Carbon Nanotubes by the metallocene route, Chemical Physics. Letters, 1997, **267**, 276-280.

[12] O. Zietz, S. Olson, B. Coyne, Y. Liu, J. Jiao, Characterization and manipulation of carbon precursor species during plasma enhanced chemical vapor deposition of graphene. Nanomaterials (Basel, Switzerland), 2020, **10(11)**, 2235.

[13] P. Nikolaev, M. Bronikowski, R. Bradley, F. Rohmund, D. Colbert, K. Smith, and R. Smalley, Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide, Chem. Phys. Lett, 1999, **313**, 91-97.

[14] N. Li, X. Chen, L. Stoica, W. Xia, J. Qian, J. Abmann, W. Schuhmann, and M. Muhler, The catalytic synthesis of three-dimensional hierarchical carbon nanotube composites with high electrical conductivity based on electrochemical iron deposition, Advanced. Materials, 2007, **19(19)**, 2957-2960.

[15] S. Okubo, T. Sekine, S. Suzuki, Y. Achiba, K. Tsukagoshi, Y. Aoyagi, and H. Kataura, Purification of Single-Wall Carbon Nanotubes Synthesized from Alcohol by Catalytic Chemical Vapor Deposition, Japanese Journal of Applied Physics, 2004, **43(3)**, 396-398.

[16] K. Awasthi, R. Kumar, H. Raghubanshi, S. Awasthi, R. Pandey, D. Singh, and O. Srivastava, Synthesis of nano-carbon (nanotubes, nanofibres, graphene) materials, Bulletin of Materials Science, 2011, **34(4)**, 607-614.

[17] G. Elsa, O. Casanova, M. Román, A. Aguilar, and F. Espinosa, Synthesis of Carbon Nanotubes of Few Walls Using Aliphatic Alcohols as a Carbon Source, Materials, 2013, **6(6)**, 2534-2542.

[18] B. J. Kahdum, E. S. Abood, A. S. Abed, Multi-walled carbon nanotubes synthesis from ethanol and 2-Propanol by chemical vapor deposition, Egyptian Journal of Chemistry, 2022, **65(6)**, 1-2.

[19] E. F. Sheka, Y. A. Golubev, N. A. Popova, Graphene domain signature of Raman spectra of sp2 amorphous carbons, Nanomaterials, **10(10)**, 2021.

[20] F. Islam, A. Tahmasebi, B. Moghtaderi, J. Yu, Structural investigation of the synthesized few-layer graphene from coal under microwave, Nanomaterials, 2021, **12(1)**, 57.

[21] E. D. Dikio, N. D. Shooto, F. T. Thema, A. M. Farah, Raman and TGA Study of Carbon Nanotubes Synthesized Over Mo/Fe Catalyst on Aluminium Oxide, Calcium Carbonate and Magnesium Oxide Support, Chem Sci Trans, 2013, **2**, 1160-1173.

[22] K. Nishimura, N. Okazaki, L. Pan and Y.Nakayama, In Situ Study of Iron Catalysts for Carbon Nanotube Growth Using X-Ray Diffraction Analysis, Japanese Journal of Applied Physics, 2004, **43(4A)**, 471–474.

[23] S. Capula, K. Aguir, F. Cervantes, L. Villa, J. A. Moncayo, and Vicente G. Febles, Ozone Sensing Based on Palladium Decorated Carbon Nanotubes, Sensors, 2014, **14**, 6806-6818.

[24] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsisa and C. Galiotis, Chemical oxidation of multiwalled carbon nanotubes, Carbon, 2008, **46**, 833- 840.

[25] S. Griger, I. Sands, Y. Chen, Comparison between Janus-Base Nanotubes and Carbon Nanotubes: A Review on Synthesis, Physicochemical Properties, and Applications, International Journal of Molecular Sciences, 2022, **23(5)**, 2640.

[26] H. Koji, Y. Kusumoto, A. Hatta, H. Furuta, Formation of thermally stable, high-areal-density, and small-diameter catalyst nanoparticles via intermittent sputtering deposition for the high-density growth of carbon nanotubes, Nanomaterials, 2022, **12(3)**, 365.

[27] J. J. Guzmán-Mendoza, D. Chávez-Flores, S. L. Montes-Fonseca, C. González-Horta, E. Orrantia-Borunda, B. Sánchez-Ramírez, A Novel method for carbon nanotube functionalization using immobilized candida

antarctica lipase, Nanomaterials, 2022, **12(9)**, 1465.

[28] K. Wojtera, M. Walczak, L. Pietrzak, J. Fraczyk, L. Szymanski, A. Sobczyk-Guzenda, Synthesis of functionalized carbon nanotubes for fluorescent biosensors, Nanotechnology Reviews, 2020, **9(1)**, 1237-1244.

[29] M. A. Abu-Dalo, M. A. Al-Atoom, M. T. Aljarrah, B. A. Albiss, Preparation and characterization of polymer membranes impregnated with carbon nanotubes for olive mill wastewater, Polymers, 2022, **14(3)**, 457.

[30] A. F. Halbus, H. I. Ismael, T. A. Alalwani, S. J. Baqir, Z. H. Athab, A. J. Atiyah, S. H. Kadhim, E. J. Mohammad, Fabrication of carbon nanotube (CNTs)/Co_3O_4-Ni_3O_4/Al_2O_3 nanocomposite catalyst and its application for photocatalytic removal of Celestine blue dye, Egyptian Journal of Chemistry, 2022, **65(6)**, 1-2.

[31] D. S. Ahmed, A. L. Abed, Controlled surface modification of CNTs using mild acids through powerful sonication technique, Acta Physica Polonica, 2018, **134**, 7-9.