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Carbon Nanotubes: Synthesis via Flame Fragment Deposition (FFD) Method from Liquefied Petroleum Gas

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Abstract:

The current study uses the flame fragment deposition (FFD) method to synthesize carbon nanotubes (CNTs) from Iraqi liquefied petroleum gas (LPG), which is used as a carbon source. To carry out the synthesis steps, a homemade reactor was used. To eliminate amorphous impurities, the CNTs were sonicated in a 30 percent hydrogen peroxide (H_2O_2) solution at ambient temperature. To remove the polycyclic aromatic hydrocarbons (PAHs) generated during LPG combustion, sonication in an acetone bath is used. The produced products were investigated and compared with standard Multi-walled carbon nanotube MWCNTs (95%), Sigma, Aldrich, using X-ray diffraction (XRD), thermo gravimetric analysis (TGA), Raman spectroscopy, scanning electron spectroscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and Transmission Electron Microscopy (TEM). Under the applied experimental circumstances, the obtained characterization data confirm the synthesis of multi-wall carbon nanotubes (MWCNTs) with portion from few wall carbon nanotubes (FWCNTs). The average diameter of synthesized Carbon nanotubes ranged from 31.26 to 78.00 nm, with a purity of more than 65 percent.

Keywords: Carbon nanotubes, flame fragment deposition, Hydrogen peroxide, liquefied petroleum gas, PAHs.

Introduction:

Carbon nanotubes are ~~a~~ nanostructured form of carbon atoms that are arranged as graphite sheets wrapped in a seamless cylinder coil with a hollow core [1,2] . The number of graphitic plates in the wall distinguishes carbon nanotubes in general. Thus, single-walled carbon nanotubes (SWCNTs) with only one of the graphite layer, whereas two-walled carbon nanotubes are made up of two layers (DWCNTs). They are called multi-walled carbon nanotubes if they have three or more layers [2-4]. Carbon nanotubes have high thermal and electrical conductivity, good chemical stability, and excellent mechanical properties due to the unique arrangement of carbon atoms. Carbon nanotubes are thus a desirable material for sensors, field emission displays, hydrogen storage media, conductive and high-strength composites, nanometer-sized semiconductor devices, and solar cells [5,6,7]. Methane, ethylene, acetylene, natural gas, and other carbon sources can be used to make carbon nanotubes. These sources can create carbon nanotubes with varied morphologies, sizes, and purity [8]. When compared to inexpensive fuels like natural gas, LPG, and water gas, using pure carbon resources are highly expensive and have a limited supply [9]. Liquefied petroleum gas is the most prominent alternative carbon source. It is made up of a mixture of light hydrocarbons, primarily propane and butane, with a trace of sulfur. One of the benefits of this gas is that it is used as a carbon source, making it easily available on the market, and its price is much lower than that of other pure carbon sources [8].

Carbon nanotubes can be created using ~~a~~ variety of techniques, including laser ablation LA, arc discharge AD, chemical vapor deposition (CVD) and flame fragments deposition (FFD) [10,11]. Most CNT synthesis procedures result in CNTs that are combined with graphitic nanoparticles, catalytic particles, and amorphous carbon are examples of

amorphous and crystalline impurities. Depending on the synthesis procedure, the nature and degree of contaminants varies. Purification is the process of removing contaminants from produced goods [12]. Chemical treatment, dry oxidation, and wet oxidation are common purification processes, followed by filtration and annealing [13-15].

The current project would include employing the flame fragments deposition (FFD) method to create carbon nanotubes without the usage of a catalyst. To assure the removal of any organic residue left over from the spent LPG gas, purification methods would comprise H_2O_2 oxidation followed by acetone purification.

Materials and Methods:

The following materials were used in this research in order to prepare carbon nanotubes from liquefied petroleum gas, which was sourced from Iraq, was acquired on the Babylon Governorate's local market. In this investigation, acetone (99 percent) from S.D. Fine-chem. Ltd., City, India. The N_2 (99.99 percent) gas, was supplied by Emirates Industrial Gases in Dubai, , hydrogen peroxide (30 percent H_2O_2) from Barcelona, Scharlab, Spain were used and Multi-walled carbon nanotube MWCNTs(95%), Sigma ,Aldrich.

Methods:

The method of Flame Fragment Deposition (FFD) was utilized, with a home-built chamber equipment for the production of carbon nanotubes (CNTs) utilizing LPG, which is used as a carbon source [16,17], the production of carbon nanotubes in this method occurring without using any types of catalyst. Schematic description of this unit is shown in Fig. 1. The method used in the purification of the CNTs that have been synthesized in this section is a modification of the method described in previous work [11]. Purification of the CNTs that have been synthesized was accomplished in this manner by calcination at 350 C for 2 hours, followed by oxidation with hydrogen peroxide H_2O_2, followed by treatment with acetone. In this method, an ultrasonic water bath was used to disperse for one hour 100 mg of synthesized CNTs in 50 mL of H_2O_2. The mixture was chilled for 24 hours at 4 degrees Celsius before being brought to room temperature and gradually heated to 50 degrees Celsius until all hydrogen peroxides had been extracted. After that, the solid was rinsed with deionized water and dried for 6 hours at 80 degrees Celsius. The CNTs were then dispersed in 15 mL of acetone and sonicated for 15 minutes before being treated with acetone. For 15 minutes, the obtained suspension was centrifuged. The obtained solid was dried overnight at 100^0C , then characterized and comparison with standard CNTs (MWCNTs(95%), Sigma ,Aldrich) by using X-ray diffraction (XRD), thermo gravimetric analysis (TGA), Raman spectroscopy, scanning electron spectroscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and transmission electron microscopy (TEM) .

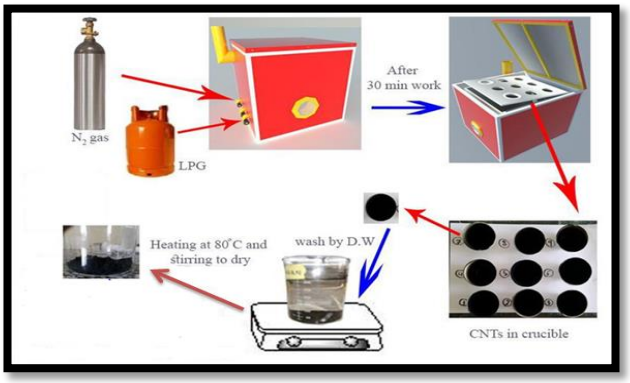

Figure 1. Schematic diagram of the steps used by the Flame Fragmentations Deposition Instrument (FFD) to synthesize CNTs.

Results and Discussion:

SEM was used to examine the surface morphology of the synthesized CNTs. This method primarily provides information on the sample's surface shape as well as its chemical composition. The images in Fig. 2 show the formation of carbon nanotubes clearly and a homogeneous distribution of synthesized CNTs with an average diameter ranging from 31.26 to 78.00 nm, while the average diameter of standard CNTs ranges from 51.55 nm to 83.82 nm, as shown in Fig. 3. TEM pictures Fig. 4 shows of as-grown carbon nanotubes, which provide a more realistic representation of the synthesized tubular structure. The nanotubes in the TEM image are 29 to 55.5 nanometers in diameter. This indicates that the synthesized CNTs falls within the range of MWCNTs specifications. Using energy-dispersive X-ray spectroscopy (EDX), the elemental composition of the synthesized CNTs was investigated. Figure 5 depicts the obtained results; Fig. 6 shows that of standard CNTs, for comparison. These findings support the oxygen, iron, and carbon content of the synthesized CNTs and starting materials. The quantitative analysis shows the content ratio of the synthesized CNTs, which yielded 89.1% of C, 6.9% of Fe, and 4% of O, while the standard CNTs yielded 93.9% of C, 2.4 % of Fe, and 3.7 % of O. This indicates that dominant element in the synthesized samples is C, as required. The crystalline nature and quality of nanotubes derived from unfavorable carbon

materials are investigated using XRD patterns. Figs. 7,8 depict XRD patterns for the synthesized and standard CNTs . From these patterns , the peak at (26.0°) for synthesized CNTs and the peak at (25.92º) for standard CNTs (MWCNTs , Sigma - Aldrich) are a typical graphitic peak caused by the presence of carbon atoms in the tubular structure in the samples, corresponding to the (002) reflection . The broad weak peaks around (43.5°) and (53.92º) for synthesized CNTs and the brood weak peaks around (43.46º) and (53.42º) for standard CNTs are attributed to the nanotube structure's (101) and (004) planes, respectively [18-20]. These results of XRD patterns for the synthesized CNTs, indicate that they are of the MWCNT type due to the convergence of the results and the features of standard MWCNTs , with very slight deviations in the positions of the peaks, possibly due to the difference in the method and conditions of preparation. Figs 9,10 show the Raman spectra of the synthesized and standard CNTs . The main peaks in these spectra are in the D and G bands: at 1321 and 1550.7 cm^{-1}; respectively for the synthesized CNTs and at 1354.25 cm^{-1} and 1551.39 cm^{-1} respectively for the standard CNTs. The D band is associated with disordered carbon atoms of CNTs that are sp^3 hybridized, whereas the G band is associated with carbon atoms that are sp^2 hybridized [21]. The second-order harmonic (the G^- band) is clearly visible at 2661.43 cm^{-1} for synthesized CNTs but equal to 2659 cm^{-1} for standard CNTs , whereas other distinguishable features of MWCNTs, such as the G+D band at 2930 cm^{-1}, are not visible, indicating a very weak band [22,23]. The ID/IG ratio is commonly used to evaluate the structures of carbon nanotube surfaces, which is the most important phenomenon of CNTs with varying amounts of defects. The ID/IG ratio of the synthesized CNTs is relatively high at (0.65), and it is equal to (1.11) for standard CNTs . The presence of a low density of defects on the tubes' walls accounts for this observation. The higher intensity of the G band compared to the D band is most likely due to the lower number of graphene layers, indicating the borderline between few-walled and multi-walled graphene. The Raman spectrum applies to single-walled and multi-walled carbon nanotubes [21,24-26].

The thermal gravimetric analysis (TGA) of the produced CNTs is shown in Fig. 11. The TGA analysis results for the synthesized CNTs after purification show that there are three main regions for losing weight. The first weight loss region appears around 100 C˚ representing a loss of around 4%. This can be attributed to the loss of water that may have been adsorbed at the surface of CNTs during purification processes conducted under normal atmospheric conditions. The second weight loss appears around 130-190 ℃, referring to a weight loss of around 2%, which can be attributed to the loss of absorbed aromatic molecules that may be presented with the liquefied petroleum gas. The third weight loose appears at 200-320 C˚ referring to a weight percentage loss of 5% of the sample's weight. This is due to the conversion of amorphous and unconverted carbon to CNTs. The largest loose occurs at 450 ℃, with a gradual decrease in weight until it reaches approximately 750 ℃, which is attributed to the degradation of graphene walls of tubular structure, with interference between each ether causing this behavior. Fig. 12 shows the TGA of standard CNTs, and the result refers to a small weight loss from (150-170) ℃, which is due to the decomposition of residual hydrocarbon impurities that are equal to 5% of the total weight. The dominant weight loss of 85% is due to the decomposition of the CNTs in the temperature range of (233-845) ℃.

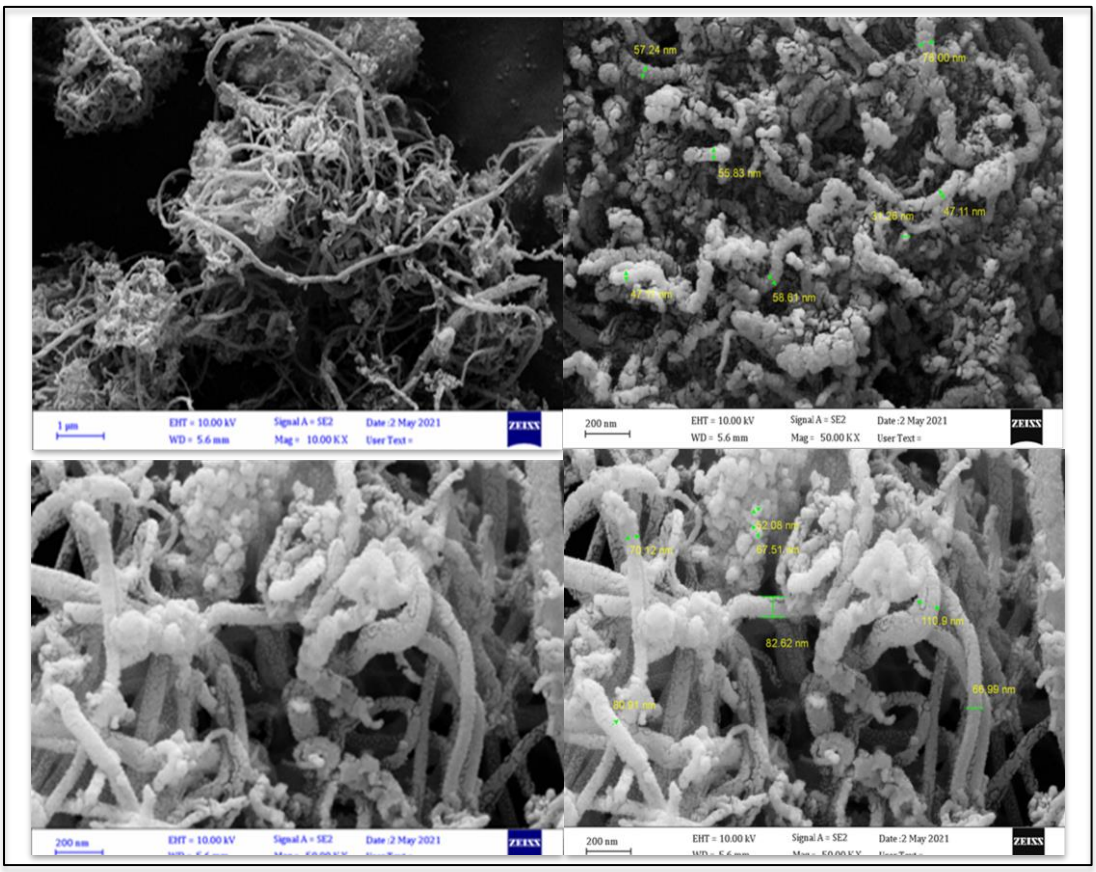

Figure 2. SEM images for the synthesized CNTs by FFD.

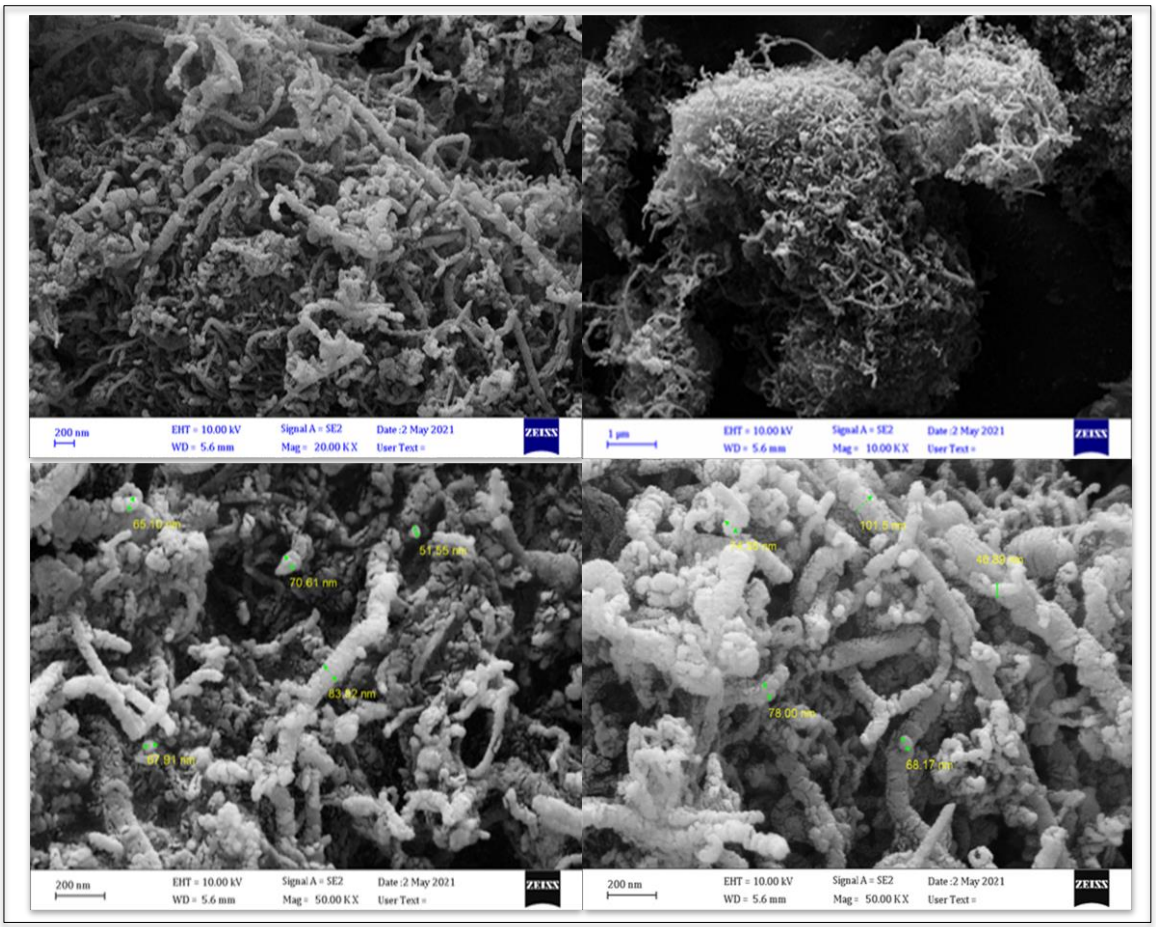

Figure 3. SEM images for the standard CNTs (Sigma, Aldrich).

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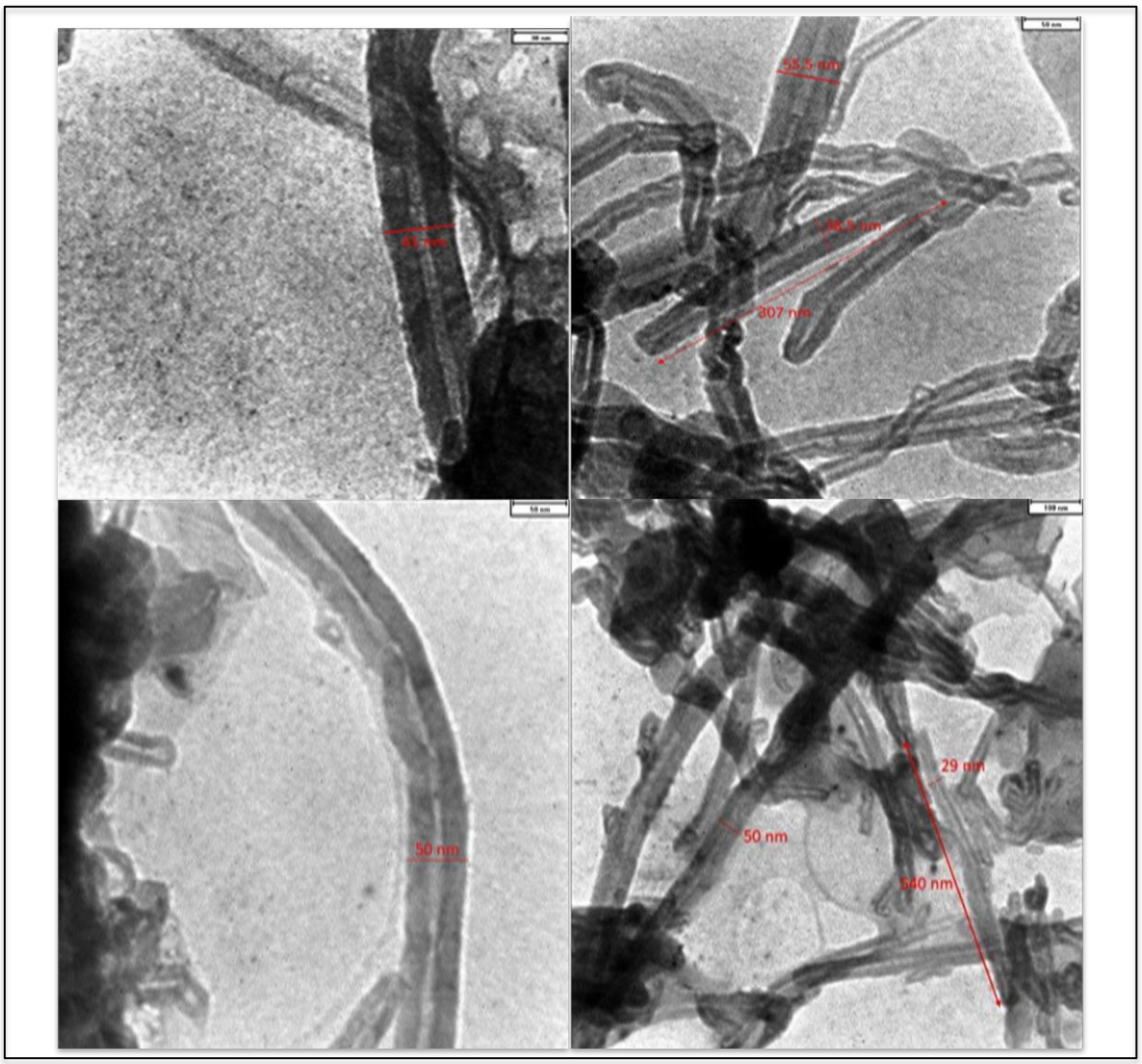

Figure 4. TEM images of synthesized CNTs by FDD

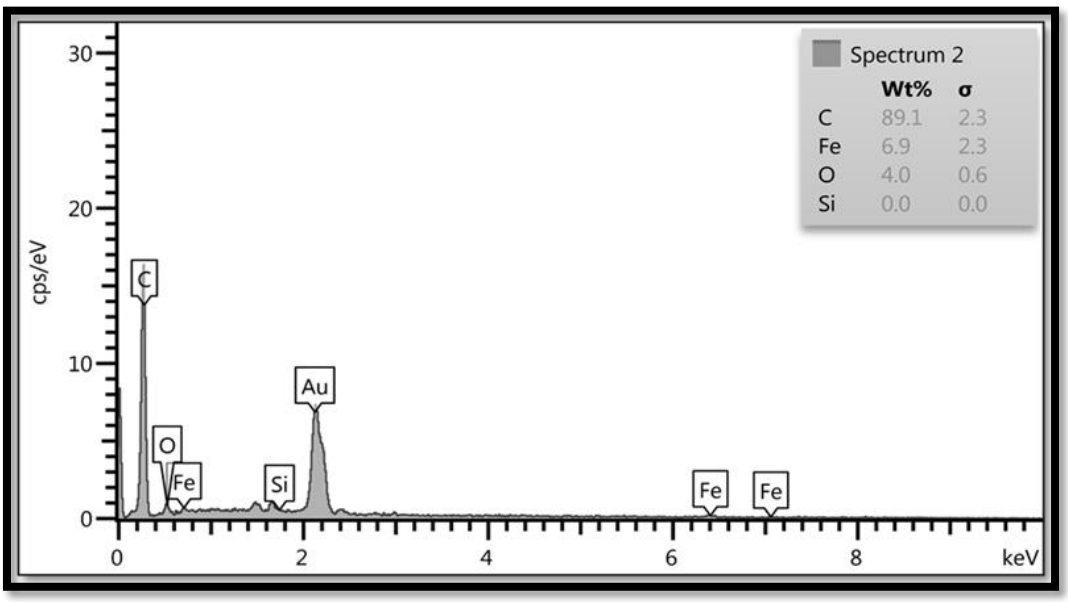

Figure 5. EDX analysis for synthesized CNTs.

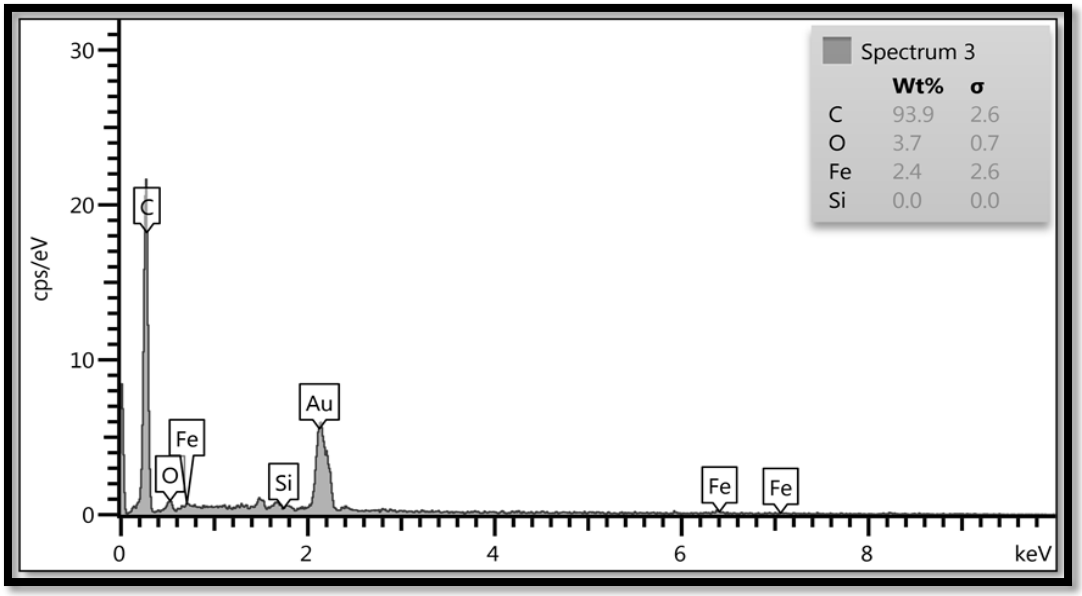

Figure 6. EDX analysis for standard CNTs.

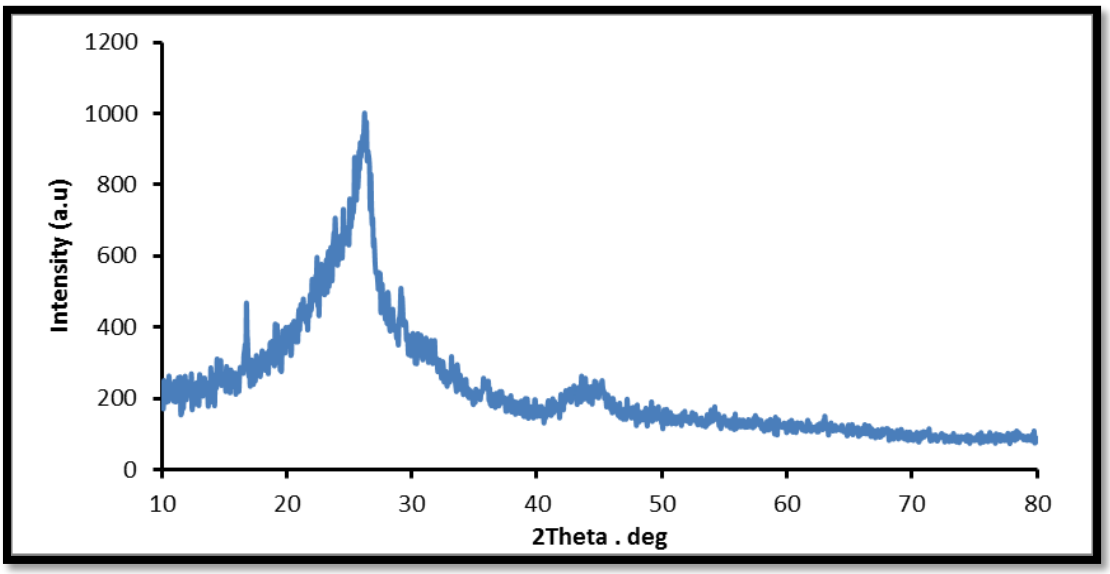

Figure 7. XRD pattern of the synthesized CNTs using FFD method.

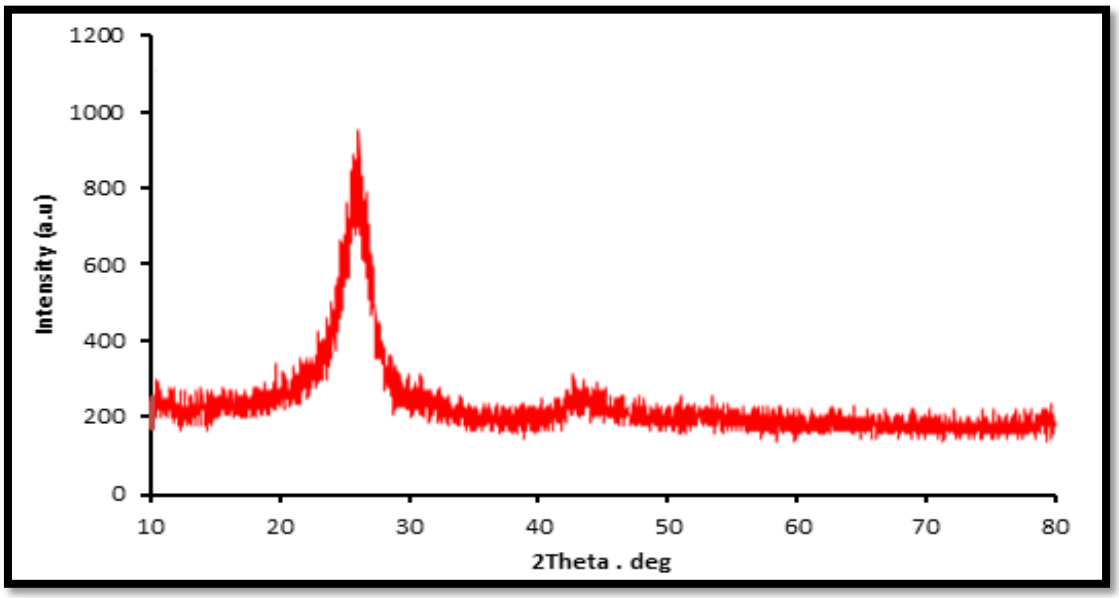

Figure 8. XRD pattern of the standard CNTs.

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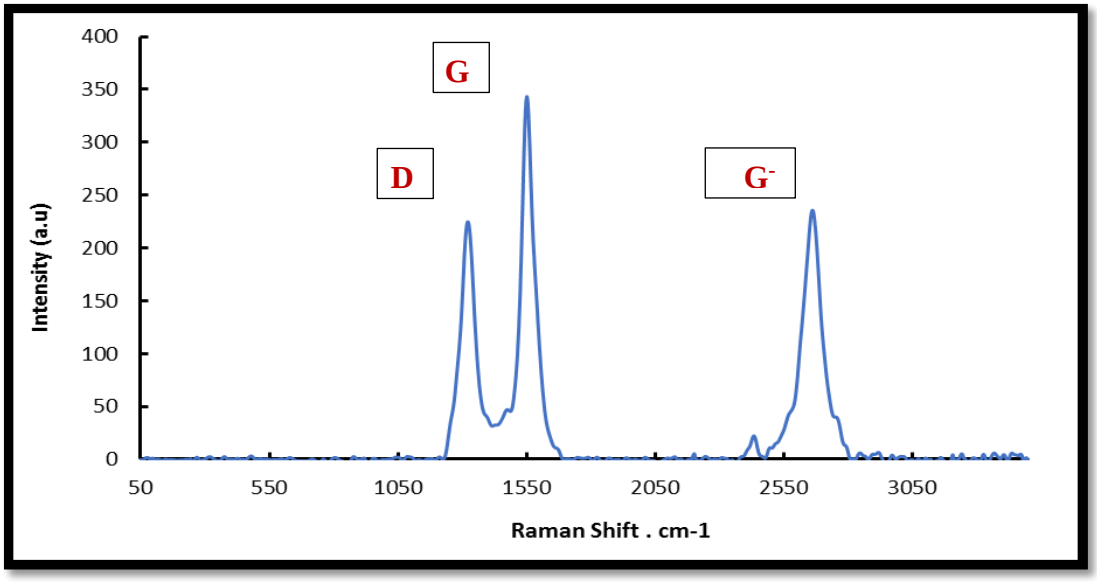

Figure 9. Raman spectrum for the synthesized CNTs.

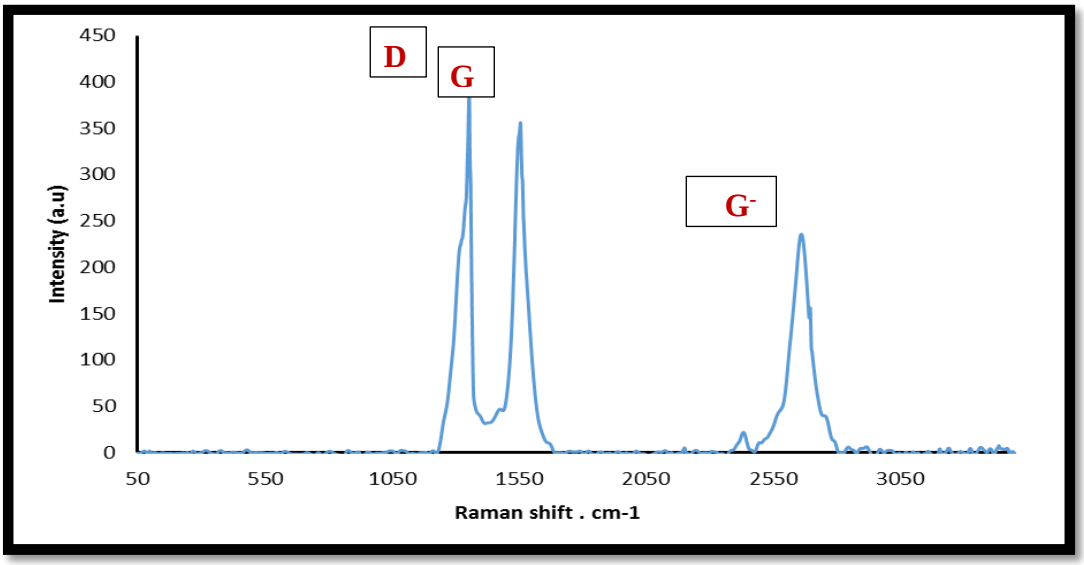

Figure 10. Raman spectrum for the standard CNTs.

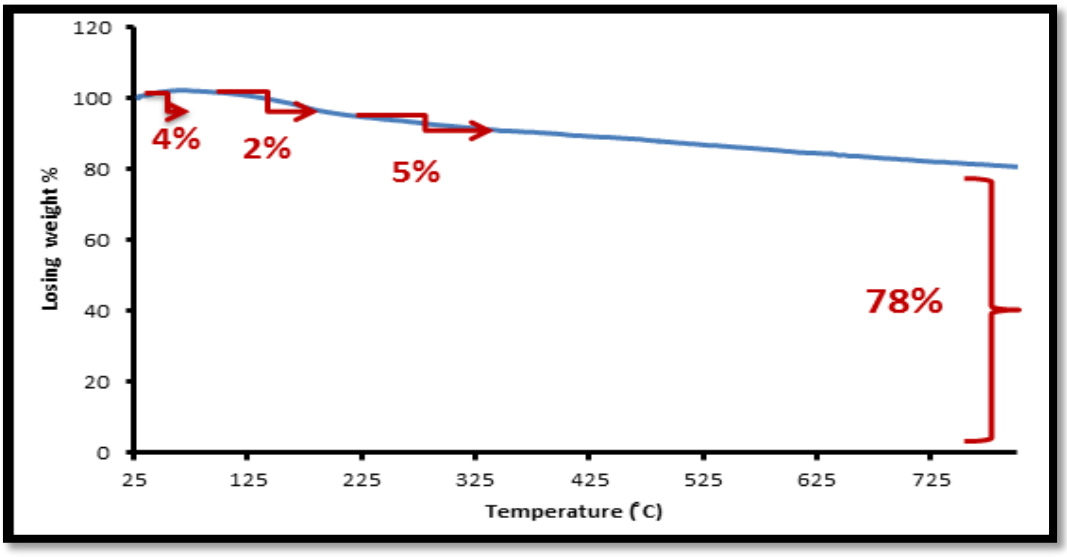

Figure 11. Schematic diagram of TGA for synthesized CNTs.

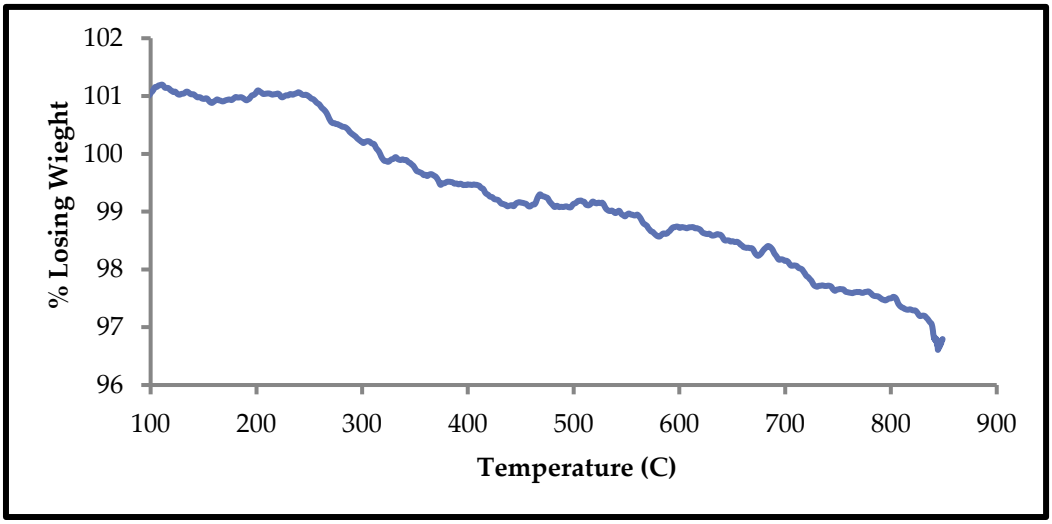

Figure 12. Schematic diagram of TGA for standard CNTs.

Conclusion:

CNTs were successfully synthesized from Iraqi petroleum gas in the current study using a homemade reactor. The flame fragment deposition method was used to make CNTs. Multiple techniques were used in order to examine and diagnose the formed material and compare it with a standard Multi-walled carbon nanotube MWCNTs(95%), Sigma, Aldrich, and the Raman spectrum results revealed that multi-wall carbon nanotubes (MWCNTs) with a percentage of few wall carbon nanotubes were formed (FWCNTs). SEM and TEM images appear the formation of nanotube.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Babylon.

Authors' contributions statement:

Work idea by F. H. H., writing the introduction and arrangement of the research was done by F. H. H. and S. S. M., the results and discussion were written by S. S. M. and F. H. H., correction done by Abbas J. The illustrations were written by Samaa S Mahmood and modified by F. H. H.. The conclusions were written by F. H. H. and Abbas J Atiyah

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الأنابيب النانوية الكربونية: التحضير عن طريق طريقة ترسيب شظايا اللهب (FFD) من غاز البترول المسال

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الخلاصة:

تستخدم الدراسة الحالية طريقة ترسيب شظايا اللهب (FFD) لتخليق الأنابيب النانوية الكربونية (CNTs) من غاز البترول المسال العراقي (LPG) كمصدر للكربون. تم استخدام مفاعل محلي الصنع لتنفيذ إجراءات التحضير. للتخلص من الشوائب غير المتبلورة، تم صوتنة الأنابيب النانوية الكربونية في محلول بيروكسيد الهيدروجين (30% wt H_2O_2)في درجة حرارة الغرفة ، متبوعًا بالصوتنة في حمام الأسيتون لإزالة الهيدروكربونات العطرية متعددة الحلقات (PAHs) المتولدة أثناء احتراق غاز البترول المسال. تم فحص الناتج المحضر، ومقارنته مع انابيب كربونية متعددة الجدران قياسية (Aldrich) Sigma ,MWCNTs(95%) باستخدام حيود الأشعة السينية (XRD) ، مطيافية رامان، التحليل الحراري الوزني (TGA) ، مطيافية الأشعة السينية المشتتة للطاقة (EDS) ، المسح الطيفي الإلكتروني (SEM) ، والمجهر الإلكتروني النافذ (TEM). في ظل الظروف التجريبية المطبقة، تؤكد نتائج التحضير التي تم الحصول عليها تخليق الأنابيب النانوية الكربونية متعددة الجدران (MWCNTs) مع نسبة من الأنابيب النانوية الكربونية قليلة الجدران (FWCNTs). للأنابيب النانوية الكربونية بنقاوة تزيد عن 65 في المائة وبمتوسط قطرها يتراوح من 31.26 إلى 78.00 نانومتر.

الكلمات المفتاحية: الأنابيب النانوية الكربونية، ترسب شظايا اللهب، بيروكسيد الهايدروجين، غاز البترول المسال، PAHs.