Comparison between Chemical Vapor Deposition and Flame Fragments Deposition Techniques for Synthesizing Carbon Nanotubes

Firas H. Abdulrazzak[1*], Ahmed M. Abass[2], Ayad F. Alkaim[3], Falah H. Hussein[4]

Abstract

Chemical vapor deposition (CVD) and flame fragments deposition (FFD) are two techniques to synthesize CNTs from propanol and liquefied petroleum gas (LPG) respectively. The two synthesized CNTs were analyzed by using high resolution-transmission electron microscopy HR-TEM in order to make compare between the two types CNT/CVD and CNT/FFD. The HR-TEMs images showed that the two types were few walled carbon nanotubes FWCNTs with 0.6-1.2 μm and 1.1- 2.7 μm in length for CNT/CVD and CNT/FL respectively. The outer and inner diameter were referred to thickness 2- 4 sheet of graphene for CNT/CVD while CNT/FFD was 2-3 sheets of graphene. The analysis indicates that Raman spectroscopy were influence with impurities when shows reduceing in the intensities of G, D and RBM bands.

Key Words: CNTs, CVD, FFD, HR-TEM, FWCNT.

DOI Number: 10.14704/nq.2020.18.4.NQ20154 **NeuroQuantology 2020; 18(4):05-10**

Introduction

Carbon nanotubes CNTs after 29 years for the first publish papers by Iijima [1] was become one of the most common nanomaterial NMs using and applying in most of advance labs. Despite many researchers classified CNTs know as classic NMs but, physical and chemical behavior for CNTs did not prevent to continue huge attempts for different applications [2]. The multiplicity in Preparation techniques and purification, still the trend to increase the selectivity and sensitivity for quantities and qualities of synthesize [3]. The right chooses for CNTs types absolutely led to ideal or maximum benefit for applications which, requires use the best method for preparation. CVDs require insertion substrate in gases phase with carrier gas such Ar or N_2 then precipitated on support surface at the lower part of tube furnace with or without catalyst at high temperature generally more than 600°C [4].

Flame method FL needed for gas, liquid or solid state can ignition in simple conditions which precipitate on the upper part of reactors [5]. FLs required oxidized the hydrocarbons with O_2 to produce gaseous mixture such carbon monoxide and dioxide, water vapor, hydrogen and free radicals of fragments hydrocarbons. The two species Hydrocarbons with carbon monoxide responsible on solid carbon deposited to form CNT/FL. The most important characteristic FLs vs CVs, is the first rich in high concentrations intermediate radicals of gas-surface that applied to heterogeneous kinetics interactions [6].

Corresponding author: Firas H. Abdulrazzak
Address: 1*Department of Chemistry, College of Education for Pure Science, University of Diyala, Diyala, Iraq; 2Department of Chemistry, College of Education for Pure Science/ Ibn Al-Haytham, University of Baghdad, Baghdad, Iraq; 3Department of Chemistry, College of Science for Women, University of Babylon, Hilla, Iraq; 4Department of Pharmaceutics, College of Pharmacy, University of Babylon, Hilla, Iraq; 4Department of Research and Studies, Al-Mustaqbal University College, Babylon, Iraq.
Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
Received: 08 March 2020 **Accepted:** 06 April 2020

In this work, the highlight concern with make compare between two methods for synthesis CNTs by chemical vapor deposition CVD and flame deposition FL. May be we had different in sources of carbon, conditions of precipitations and method of preparation which produce variance in product, but they produce CNTs. The different in synthesized CNTs were included length, diameters structure and by product, which characterized by transmission electron microscopy TEM.

Experimental

Materials

Propanol was equipped from Alfa, Aesar with purity 99.5%. Iraqis liquefied petroleum gas was supplied from local markets in Iraq, physical and chemical properties were analysis in petroleum research and development center, which reported in our previous work [5]. Hydrogen peroxide H2O2 was purchased from Spain 30% percent weight for purification process. Ferrocene were purchased from Sigma. Nitrogen gas with purities 99.999% was purchase from Emirates industrial gases.

Process of Synthesis CNTs

1. Chemical vapor deposition unit CVDs: Fig. 1A refer to CVDs unite which include tube furnace mono stage Nabertherm USA equipped with quartz tube (100 cm in length and 5 cm diameter). Three boat made from ceramic were used as a support for catalyst which was ferrocene. N_2 gas was purges through the tube before switching on the furnace with flow rate 175 cm^3/min for 15 minutes. The furnace was switched onto 700 ºC with 4 °C/min rate of heating at atmospheric pressure. After reaching tube furnace the required temperature, propanol was starting to boil for 25 minute and reduce the flow rate of N_2 to 75 cm^3/min which still constant after stop heating and reach room temperature.
2. Flame deposition unite FDU: Fig. 1B shows skim for the reactor homemade (25cmx20cmx20cm), and laminar in the center of lower part with two sources of gases (N_2 and air). The surface of precipitation was made from iron and fixed over 5 cm of laminar which carved with ferrocene. The flow of gases was controlled by two mass flow controllers with an accuracy of ± 2.5 % (BROKER, DK800S-3) were used for liquefied petroleum gas and air.

The two samples after preparations was purified by H_2O_2 as we reported in our previous work [5] before characterized. The CNTs which produces from CVDs will be refer to it by CNT/CVD while ether will be CNT/FL respectively. The transmission electron microscopy TEM was depend on this work to explain the nature of products and make compere between CNT/CVDs and CNT/FLs.

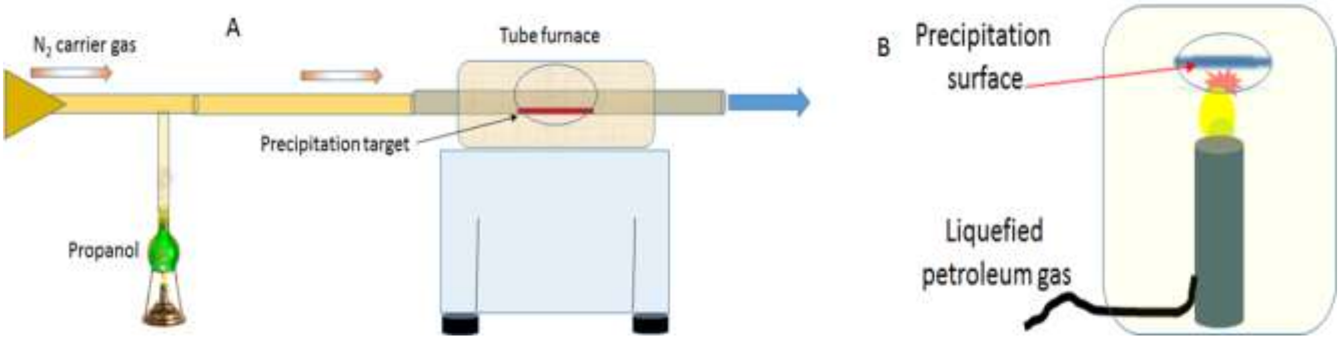

Figure 1. The skim for synthesis CNTs by (A) CVD and (B) FFD

Results and Discussion

The characterization of synthesized CNT was done when taken images with High- resolution transmission electron microscopy HR-TEM by JEM-2100F Japan**.** Raman spectroscopy were done by a SENTERRA Raman spectrometer (Bruker) and laser wavelength was 532 nm with a resolution of 1 cm^{-1} which recorded in the 200–1700 cm^{-1} spectral region at ambient temperature.

The HR-TEMs images in figure 2, 3, and 4 shows clear views for synthesized CNTs which depend to find mechanism for forming product in these two cases. It can be seen for both method from figure 2, presence of filaments structures of and unconverted carbon, look like balls structure of carbon or black carbon BC with particles of iron catalyst. Fig. 2A and B, shows High ratios of CNTs when used CVDs while a high percentage of BCs and iron were observed with low ratios of CNTs when used flame method CNT/FFD. The reduces and increase the ratios of CNTs or BCs influence directly with condition of forming tubular structure such temperature and mechanism of precipitation. The low temperature with upper direction for precipitation enhance compacting toward the quadruple stacking of sp3 forming circular structure of BCs which raise sp3/sp2 [7] with reduce CNTs that were accord with CNT/FFD. The second types CNT/CVD was forming in higher temperature which enhance forming higher ratios for sp2/sp3 [8]. Mostly the existence of impurities can be related to the low catalytic activity of particles causing remove many nucleation sites for growth CNTs [9-10] which produce at low temperature and that clear with CNT/FL. Figure 3 , include clear images for the length with inner and outer diameters of tubes which can be determined number of sheets that forming tubular structure. The length of CNTs which produce from CNT/CVD method was 0.6-1.2 μm while for CNT/FFD was 1.1-2.7 μm and that refer to double value.

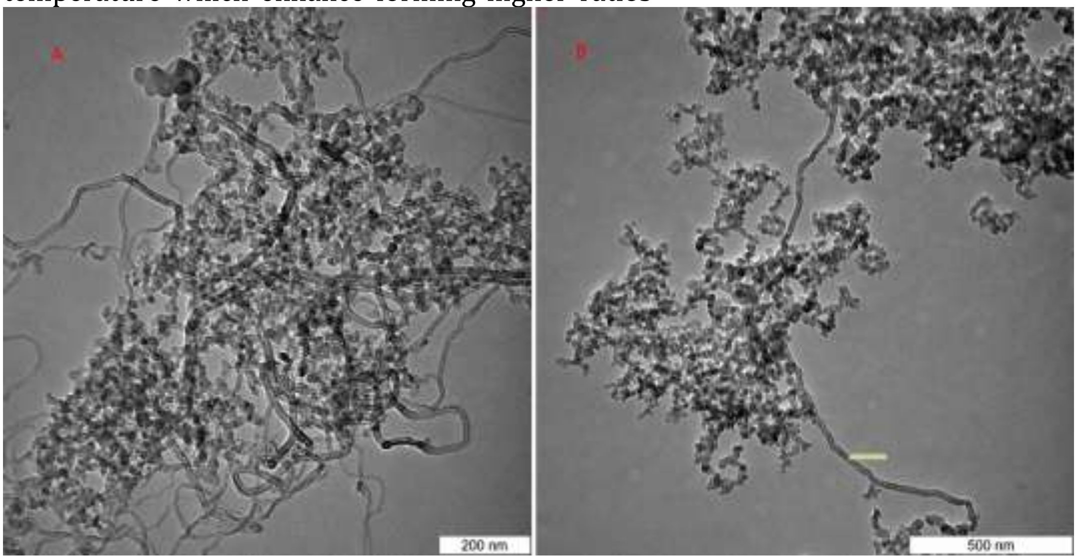

Figure 2. The HR-TEMs images for a- CNT/CVD and b- CNT/FL

The outer diameters were shown 5-9 nm with inner diameters 2.5-3.7 nm and that refer to about 2- 4 sheet of graphene thus it classified as graphene nanotubes gNTs or few walled carbon nanotubes FWCNTs. The next types CNT/FL was shown 5-7 nm for outer diameters with 2.6-2.8 nm in inner diameters which means 2-3 sheets of graphene and that also classified as FWCNTs. The measurements show higher length and homogenous structure of the wall with CNT/FFD as compare with CNT/CVD

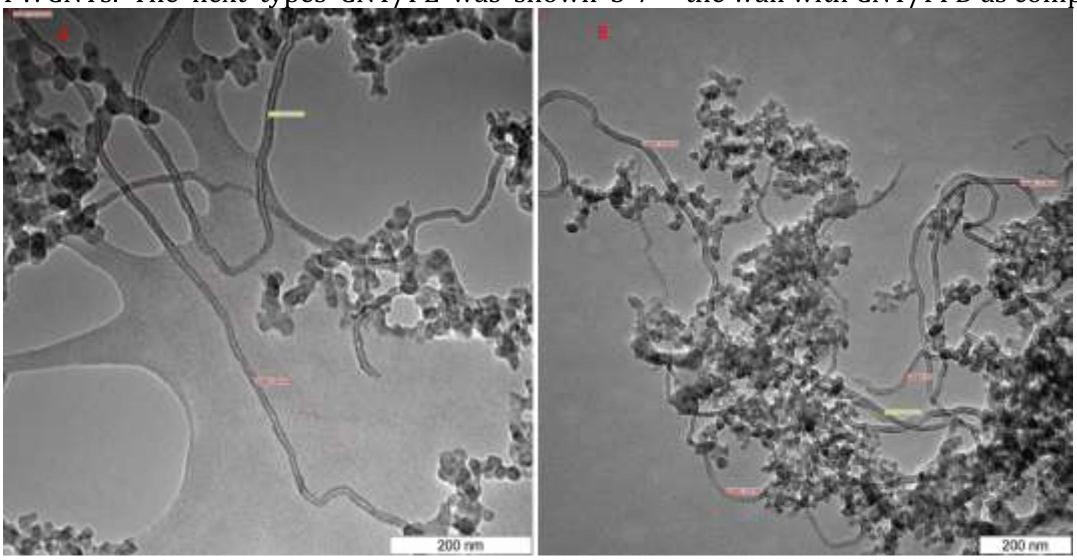

Figure 3. The HR-TEMs images to determined inner and outer with length of tubes for a- CNT/CVD and b- CNT/FFD

May be irregular distributions for catalyst on the support surface create strange filaments of carbon as compare with ether CNTs in the reactor with the two types CNT/CVD and CNT/FFD. The surprised was the nature of strange tubes was represented by very high outer diameters with different structure for the nature of growth. Figure a shows tube with 0.62 µm in length and 34 nm for outer diameter with 6 nm in inner diameter which refer to MWCNTs with 37 sheets of graphene. The surprise in figure b tube with more than 1.2 µm in length while high stacked installation with diameter reach to 34 nm without inner diameter or bore can see. The nature of tubes like successive stack in the middle tub, while at the left and right tubes it can be seen inner bore with diameter 3 and 19 nm respectively.

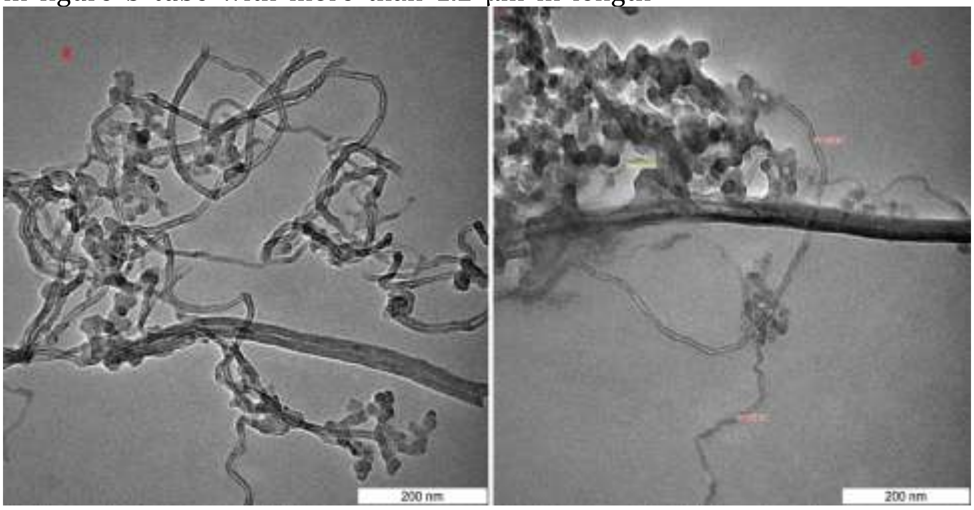

Figure 4. The HR-TEMs images for large tubular structure with a- CNT/CVD and b- CNT/FFD

The imputers such unconverted carbon and remaining catalyst and support were appears as black heterogonous particles with size 10-29 nm for CNT/CVD, while CNT/FFD were more size when shows 28- 46 nm. The three TEMs images for the two types CNT/CVD and CNT/FLFFD which shows variance in product beside the similarities in general view can be related the nature of synthesized process. Generally, mechanism of CNTs growth until know still in the range of supposing or theories view thus, many opinions and many acceptable mechanisms. The CVDs process required inter the precursor to the inner tube furnace in gas phase then convert to many free radicals' groups which precipitate after dissolved on hot surface. The hot surface with or without catalyst after reaching for saturated state, the growth of CNTs start to increase towards the upper side/reverse gravity. The last case makes the gravity responsible to decide the vertical growth causing reduce in length with CNT/CVD [11]. The vertical growth/lower direction make the increase in length towards the gravity, that meaning ''gravity'' increase the length of tubs thus CNT/FFD shows more length as compare with CNT/CVD. [11-12].

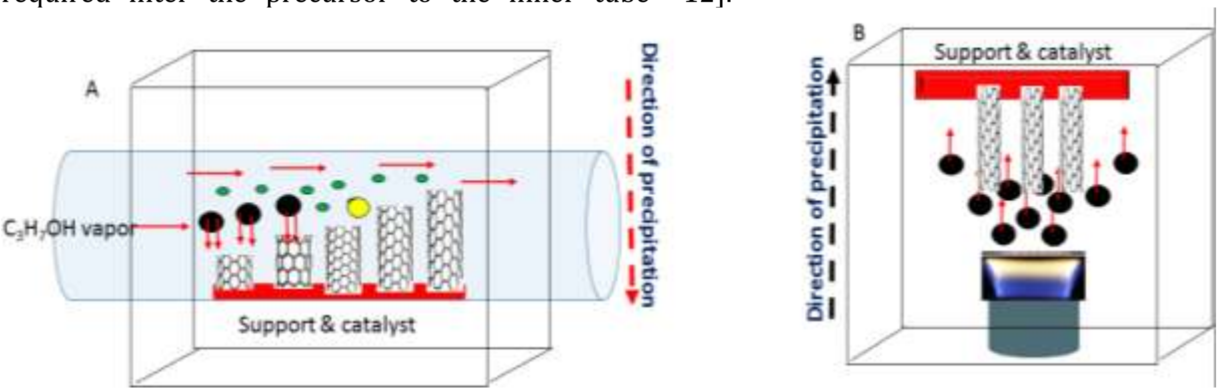

Figure 5. The skim for precipitation mechanism by (A) CVD and (B) FFD

The influence of impurities can be seen towards the function groups of the synthesized CNTs which was FWCNTs for the two types. Raman spectroscopy able to identify the active or function groups which is C=C when shows two band D and G at about 1350 cm^{-1} and 1580 cm^{-1} respectively [4]. The two band was shown variance in intensity when reduce with CNT/FFD while CNT/CVD was less influence and that can be related to impurities which interference with C=C groups as shown in figure 6. The impurities cause reduce in RBM band at range 200-560 cm^{-1} when appear with SWCNTs and FWCNTs and that again was very clear with CNT/FFD, although that include a smaller number of sheets as compare with CNT/CVD [13]

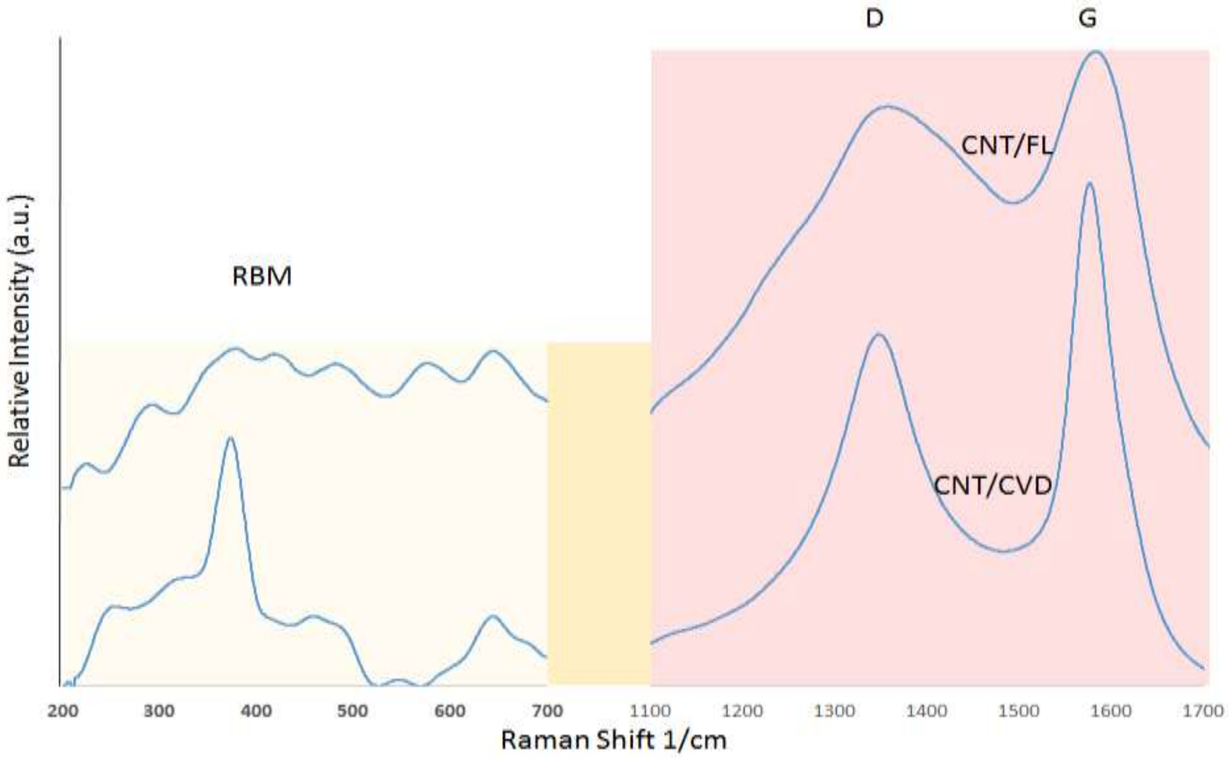

Figure 6. The Raman spectroscopy for CNT/CVD and CNT/FFD

Conclusion

CNT/CVD and CNT/FFD were synthesized successfully using two techniques from two different precursors. The CNT/FFD was longer and less inner and outer diameters with more BC and unconverted carbon as compare with CNT/CVD. The HR-TEM images refer to decrease the impurities content of products with FLs more than CVDs and that may relate to temperature of precipitation and that were influence in spectrum of Raman spectroscopy. Despite surprising results of CNTs obtained for unregulated tubes in length and diameters there are still tremendous opportunities to be explored and significant challenges to synthesis homogenous length and outer with inner diameters CNTs. Therefore, the right choses for technique, substrate, condition of preparation with ideal distribution for catalyst all of it could do that.

References

Iijima S. "Helical Microtubules of Graphitic Carbon", *Nature* 1991; 354(6348): 56-58.

Rossi MB, Faquine RK, Carvalho FB, Renata GR, Larissa AMT, Gilmar PT. Recent advances in the use of carbon nanotubes as smart biomaterials. J. Mater. Chem. B, 2019; 7(9): 1343-1360.

Prasek, J, Drbohlavova, J, Chomoucka, J, Hubalek, J, Jasek, O, Adam, V, Kizek, R. (2011). Methods for carbon nanotubes synthesis. Journal of Materials Chemistry, 21(40): 15872-15884.

Falah HH, Firas HA, Ayad FA. Nanomaterials: Biomedical and Environmental Applications, chapter 1: Nanomaterials: Synthesis and Characterization, 1ed. Welly 2018.

Abdulrazzak FH, Abbas AM, Hussein FH. Synthesis of multi-walled carbon nanotubes from Iraqi natural gas/CO mixture by catalytic flame fragments deposition method. Asian Journal of Chemistry-unify 2019; 31(1): 247-250.

Li TX, Kuwana K, Saito K, Zhang H, Chen Z. Temperature and carbon source effects on methane–air flame synthesis of CNTs. Proceedings of the Combustion Institute, 2009; 32(2): 1855-1861.

Lin Y, Sun X, Su DS, Centi G, Perathoner S. Catalysis by hybrid sp 2/sp 3 nanodiamonds and their role in the design of advanced nanocarbon materials. Chemical Society Reviews 2018; 47(22): 8438-8473.

Cartwright RJ, Esconjauregui S, Weatherup RS, Hardeman D, Guo Y, Wright E, Daniel O, Stephan H, John R. The role of the sp2:sp3 substrate content in carbon supported nanotube growth. Carbon 2014; 75: 327-334.

Gopinath P, Gore J. Chemical kinetic considerations for postflame synthesis of carbon nanotubes in premixed flames using a support catalyst. Combustion and Flame 2007; 151(3): 542-550.

Li H, Shi C, Du X, He C, Li J, Zhao N. The influences of synthesis temperature and Ni catalyst on the growth of carbon nanotubes by chemical vapor deposition. Materials letters 2008; 62(10-11): 1472-1475.

Yeh CM, Chen MY, Syu JS, Gan JY, Hwang J. Effect of gravity on the growth of vertical single-walled carbon nanotubes in a chemical vapor deposition process. Applied physics letters, 2006; 89(3): 033117.

Bati AS, Yu L, Batmunkh M, Shapter JG. Synthesis, purification, properties and characterization of sorted single-walled carbon nanotubes. Nanoscale 2018; 10(47): 22087-22139.

Braun EI, Huang A, Tusa CA, Yukica MA, Pantano P. Use of Raman spectroscopy to identify carbon nanotube contamination at an analytical balance workstation. Journal of occupational and environmental hygiene 2016; 13(12): 915-923.