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Abstract. Production of high-quality Multi-Walled Carbon Nano-Tubes (MWCNTs) is essential in some field, especially in medical and mechanical applications. This work illustrates the synthesis of high-quality (MWCNTs) by Injection Chemical Vapor Deposition (Inj-CVD) method using Ferrocene / Toluene solution as a carbon precursor and a catalyst. The effect of synthesis pyrolysis temperature, which has a pivot impact on the synthesis process, was investigated. The structure defects, impurities, thermal stability and sample morphology, as well as the mean diameters of the MWCNTs, were analyzed using Raman spectroscopy, thermal gravimetric analysis (TGA) and scanning electron microscope (SEM), respectively. The results revealed that a change in quality, mean diameter and purity were observed when the pyrolysis temperature varied between 700°C to 850°C. High-quality MWCNTs were observed by Raman spectroscopy at a pyrolysis temperature of 700°C with ID/IG = 0.2. While the outer and inner diameters were 25±6 nm and 7.8±1.5nm respectively, measured by Transmission Electron Microscope (TEM). The Inj-CVD shows an excellent control of the quality of the prepared MWCNTs by optimizing the synthesis temperature.
Keywords: High-quality Carbon Nano-tubs, Effect of temperature on CNTs, Characterization of CNTs.

1. Introduction

In recent history, Iijima's synthesized carbon nanotubes CNTs by arc evaporation method for C_{60} [1]. At the same time, a small company in the USA was already able to produce defected carbon nanotubes called carbon fibrils using a chemical vapor deposition [2]. These achievements attracted considerable attention in both the technological and scientific communities and initiated a wide range of research in several important directions [3,4]. Due to their unique properties such as mechanical[5] thermal[6], chemical [7], electrical[8], optical[9,10] and magnetic [11], carbon nanotubes are designated as one of the most attractive materials for many applications. These properties are directly affected not only by a unique structure such as (zigzag, arm-chair and chiral); but also by how the graphene sheets were rolled up. CNTs have different forms as single-walled carbon nanotubes (SWCNTs) which defined by only one rolled graphene sheet [12,13]. However, Double-walled carbon nanotubes (DWCNTs) have two rolled graphene sheets [13,14] and multi-walled carbon nanotubes (MWCNTs) have more than three rolled graphene sheets[15]. In principle, Injection Chemical Vapor deposition (Inj-CVD)[16] is considered a simple and inexpensive synthesis method for the production of MWCNTs, compared with other bottom-up methods[12,17] such as Arc-discharge [18,19] and laser ablation[20]. The evaporation of carbon atoms

from solid targets at a temperature above 3,000°C, as in Arc-discharge and laser ablation methods, is neither economical nor convenient [21]. In addition, Inj-CVD can be operated under atmospheric pressure, moderate temperatures and does not require any special substrates. Furthermore, several researchers found that CVD [22] technique gives a very low aspect ratio. (ID /IG) define this ratio, where ID is the intensity of D band, which is a characteristics band refers to disordering in carbon nanotubes structure and located in the range of 1350 cm^{-1} Raman shift. While, IG is the intensity of the G band, which is a characteristics band that refers to graphitization in carbon nanotubes structure and located around 1500 cm^{-1} Raman shift [23, 24]. This aspect ratio refers to the disorder in Carbon Nano-materials Structure (CNMs) [25,26]. The lower aspect ratio indicates the highest [24,25,27].
In this work, high-quality MWCNTs were synthesized using Inj-CVD technique using an optimum concentration of Ferrocene in the Toluene solution as a carbon precursor and a catalyst. The uniform injection feed rate of this solution was used, under Argon as a carrier gas at 1 atm (pressure) and the surface of Quartz tube as a substrate. The influence of temperature on synthesizing MWCNTs quality was investigated using Raman spectra in the frequency range of 500 –3500 cm^{-1}. The thermal stability and the purity of syntheses MWCNTs were studied by thermos-gravimetric analysis (TGA). The morphology, as well as the outer diameter of the samples, were investigated using a scanning electron microscopy (SEM). In addition, the inner and outer diameters of the prepared MWCNTs samples were visualized and confirmed with high-resolution transmitted electron microscopy (TEM).

2. Experimental

2.1. Materials and chemicals

Carbon nanotube was synthesized using materials and chemicals characterized and listed in the Table 1.

Table 1. The main Characteristics of the chemicals and material used in the synthesis of MWCNTS

No	Name	Type	Source	Melting Point˚C	Boiling point ˚C	Chemical form	Density g/cm^3	Act as
1	Toluene	Colorless liquid	Fisher Scientific, UK	-95	110-111	C_7H_8	0.87 at 25°C	Carbon precursor
2	Ferrocene	Light orange powder	Sigma-Aldrich, UK	173	249	$C_{10}H_{10}Fe$	1.49 At	Carbon precursor, Catalyst donor

2.2. Synthesis of MWCNTs experimental procedure

The injection chemical vapor deposition (InJ-CVD) method was employed to synthesize MWCNTs [28-30] in a typical experiment setup as shown in figure 1. The main tubular furnace temperature, synthesizing pyrolysis temperature, was varied from 700 to 850 ± 5 °C under the flow of argon gas at atmospheric pressure. The volume of Toluene (carbon source) and Ferrocene (carbon source and catalyst) was adjusted to 5% (w/w) by weight respectively. A 2.21 cc/h of feed solution was uniformly injected using syringe pump (Razel R99-E LF28V) to a horizontal preheated tube at a temperature of 200˚C (the evaporation temperature of Ferrocene) for 60 min. The evaporated feed is then flushed away to the main furnace by 100 cc/hr of argon (carrier gas & pyrolysis medium).

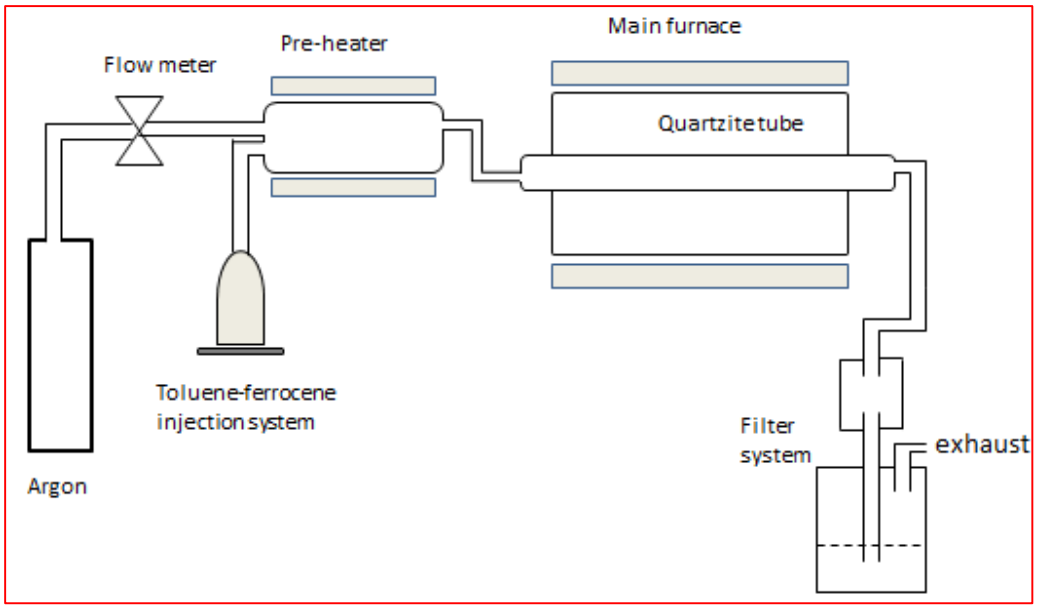

Figure 1. Schematic diagram of Injection CVD setup

2.3. Characterizations of synthesized MWCNTs

The effect of pyrolysis temperature on the type and quality of MWCNTs is investigated by measuring the Raman spectra of the samples. The results were recorded in the frequency range of 500 –3500 cm^{-1} using a Raman spectrometer (JY HR-800 type) with a laser excitation line at 532 nm and 12.5 nm power. The thermal stability of syntheses MWCNTs and the purity were studied by Thermal Gravimetric Analysis (TA55).The temperature profile starting from 30˚C to 830˚C under airflow rate 25 CC/hr with heating rate 20˚C/min. The outer diameter, as well as morphology of the samples, were investigated by scanning electron microscopy (SEM), ZEISS SEM EVO 10 MA. To visualize the high quality of prepared MWCNTs; Transmission electron microscopy (TEM) was operated at 200 kV. For this purpose, sonication of the prepared samples in ethanol was conducted and then a small droplet of the dispersion was deposited on the TEM carbon grid and dried for 10 min.

3. Results and discussion

3.1. Quality investigation using RAMAN spectroscopy

Raman spectroscopy depends on induced dipole moment, So it's sensitive to the highly symmetric covalent bonds that have not dipole moment as found in CNMs [25,31]. Therefore, the Raman spectroscopy technique is usually used to detect the type and quality of Carbon Nano-materials (CNMs). In general, CNTs with all of its types, in addition to Graphene and fullerene were identified by three main Raman peaks [32]. These peaks called D band, G band and 2D band, which appear at Raman shift around 1350cm^{-1}, 1500 cm^{-1} and 2700 cm^{-1} respectively. Figure 2 shows the Raman spectra for the prepared samples at different synthesizing temperature. Raman spectra not only used to differentiated the types of CNTs as SWCNTs, DWCNTs or MWCNTs but also can be used to measure the quality of the prepared sample [31]. The quality of CNMs was investigated by dividing the intensity of the disordered peak (ID) over the intensity of the graphitization peak (IG) [33]. In this work, high-quality CNTs were recorded below 0.7 aspect ratio ID /IG [25] as shown in figure 3. The results revealed that the change in

synthesizing temperature affect directly the quality of the prepared samples, as the aspect ratio decreased from 0.7 to 0.2 with decreasing the synthesizing temperature from 800°C to 700 °C respectively, as shown in both figures 2 and 3.
The obtained lowest aspect ratio (0.22) by this work which achieved at a synthesizing temperature of 700°C, indicating the optimum temperature of synthesizing MWCNTs with a high-obtained quality of compared to other research work [23,25,31] .Note that under previous synthesized conditions, neither MWCNTs nor CNMs formed at 650 ° C, while CMSs formed at 850 °C as shown in figure 2.

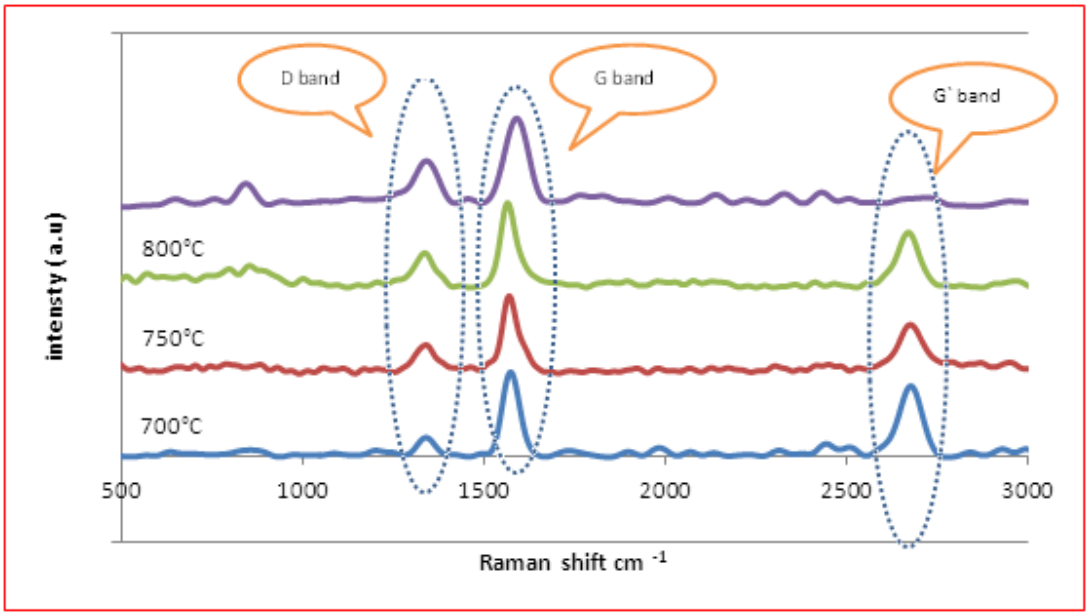

Figure 2. Raman spectra for the prepared CNMs at different pyrolysis temperature, by injection solution of 5%Wt Ferrocene in Toluene under 100cc/h argon atmosphere for 60 min.

3.2. Morphology and average outer diameter investigation using (SEM)
A scanning electron microscope (SEM) is a very important tool to show the material morphology and the outer diameter for MWCNTs. Where it can be used to estimate the average outer diameter of prepared MWCNTs. figure 4 shows the SEM images of MWCNTs samples synthesized at different pyrolysis temperatures with the same magnification which equals 35KX and tall bar equal 1µm. Under the studied experimental conditions there where no MWCNTs are formed at the temperatures range from 600 ˚C to 650 ˚C. While carbon microspheres structures are formed in the temperatures range from 850 ˚C to 900 ˚C. For the sample synthesized at 700˚C, the average outer diameter was 35±10 nm as shown in figure 4a. However, for the sample synthesized at 750˚C the average outer diameter equal to 50±16 nm figure 4b. Moreover, for the sample synthesized at 800˚C the average outer diameter equal to 75±12 nm figure 4c. While for the sample synthesized at 850˚C at the same experimental conditions, figure 4d, carbon microspheres (CMSs) was generated with average outer diameter equal 2±0.1 µm

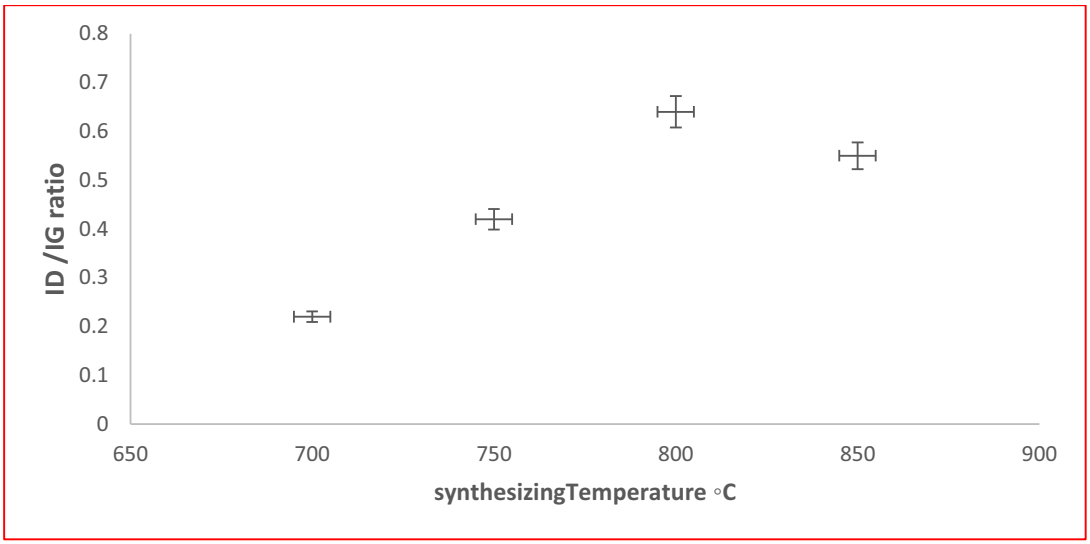

Figure 3. Raman spectra for the prepared CNMs at different synthesizing temperatures shown the quality (disordered ratio) vs. temperature

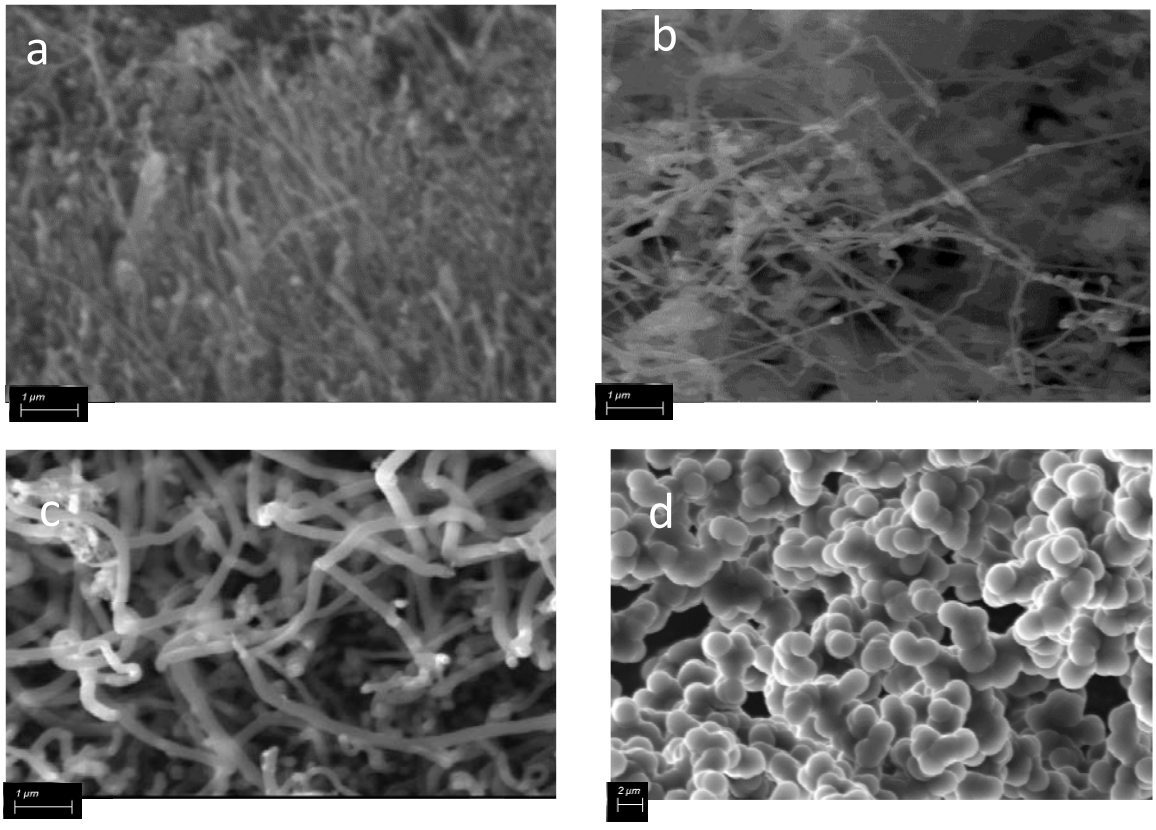

Figure 4. SEM images of MWCNTs samples synthesized at different pyrolysis temperatures: (a) 700˚C, (b) 750 ˚C, and (c) 800˚C while (d) SEM image of CMSs synthesized at 850 ˚C.

Figure 5 shows the relation between the outer diameter of the prepared samples and pyrolysis temperatures. The results confirm that the outer diameter depends strongly on the pyrolysis temperature. As the outer diameter increase with increasing the pyrolysis temperature. This could be attributed to, the increases of pyrolysis temperatures leads to increasing the catalyst particles (Iron) mobility on the quartz substrate. The lager catalyst clusters formed so the lager outer diameter synthesized.

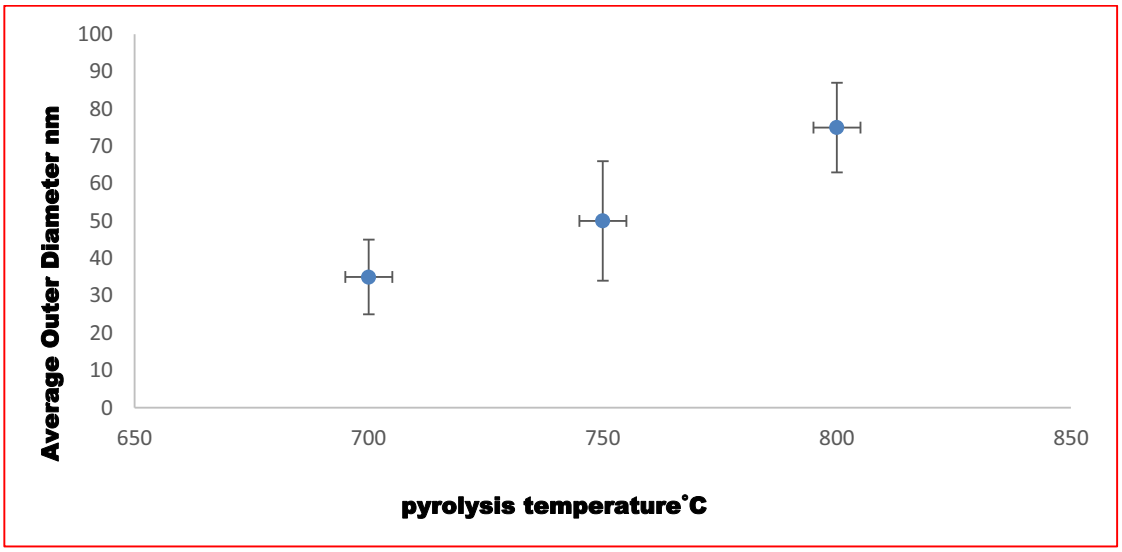

Figure 5. Average of outer Diameter for MWCNTs at 700±5˚C, 750±5˚C and 800±5˚C pyrolysis temperature

3.3. *Evaluation of dimensions of high-quality samples using (HITEM)*
High-resolution transmission electron microscope (HITEM) using to characterize the outer and inner diameter and calculate the number of tubes for MWCNTs. Here HITEM used especially to confirm that the sample synthesized at 700˚C, which had average ID/IG aspect ratio 0.22, is MWCNTs as shown in figure 6a. The averages of outer and inner diameter were 26±9 nm and 7.9±1.8 nm respectively, as shown in figure 7b. Because of the inner spacing between tunes around 0.36nm [30,34], the average number of tubes for this high-quality MWCNTs was 23±7 tube. The dark spots in both figures 6 a and b were the iron metal catalyst.

3.4. *Thermal Oxidation Stability of MWCNTs study by TGA*
In this part of the work, not only the thermal stability of syntheses MWCNTs was studied but also the purity was calculated by using Thermal Gravimetric Analysis (TGA)[35]. It has been known that the oxidation temperatures for amorphous carbon contaminants, SWCNTs, and MWCNTs are typically in the range of 200 – 300 °C, 350 – 500 °C and 400–650 °C respectively [36,37]. However, the DWCNTS bundles and bucky papers (a thin sheet made from DWCNTs) can be stable in air in the range of 500-800 °C [14,38].

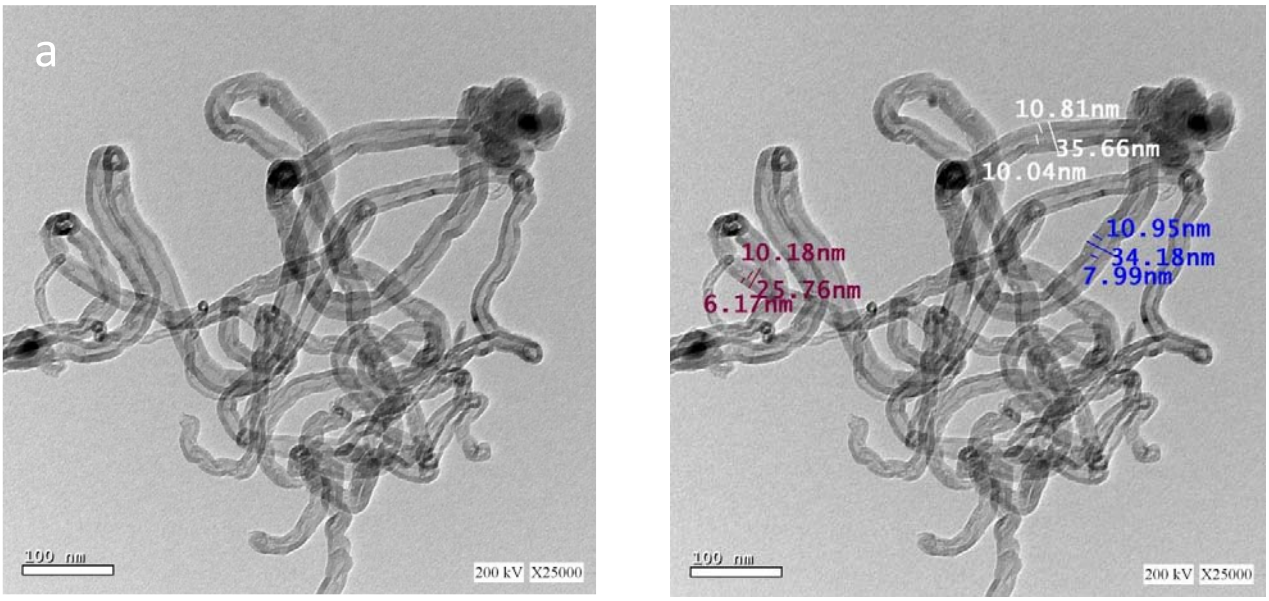

Figure 6. HITEM of MWCNTs at 700˚C with Mag=25XK (a) without diameters information and (b)with outer and inner diameters.

Figure 7 shows the thermos-gram for MWCNTs synthesized at different pyrolysis temperatures. The results revealed that in the temperature range from 200˚C to 400˚C very low weight loss was observed. This could be attributed to the prepared samples are free of amorphous carbon.

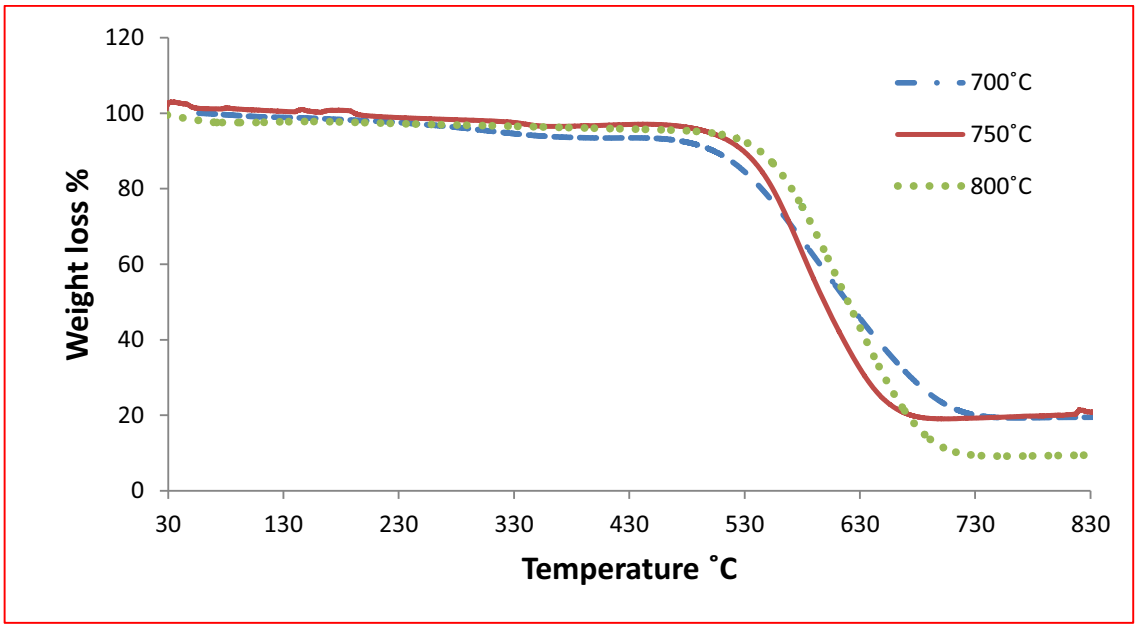

Figure 7. Thermo-gram for MWCNTs at 700˚C, 750˚C, and 800˚C pyrolysis temperature

Figure 8 shows that there is a gradually increasing in oxidation temperature from 591˚C, 594.5˚C to 613.6˚C for the sample prepared at synthesizing temperature of 700 ˚C, 750 ˚C, and 800 ˚C respectively ; which confirm that there was a relation between the synthesizing temperature and the thermal stability of the prepared samples. It indicates also, the presence of unreacted catalyst, (Fe) nanoparticles, within the prepared samples which affect its thermal stability and also its oxidation temperature value [39]. Dash line in figure 8 refers to oxidation temperature which increases with decreasing ash content (solid line). After complete oxidation of the samples, the residual mass percentage of iron oxides (ash) were 19.8±0.1, 19.5±0.1 and 10 ± 0.1 wt% for the samples prepared at synthesizing temperature 700˚C, 750˚C, and 800˚C respectively.

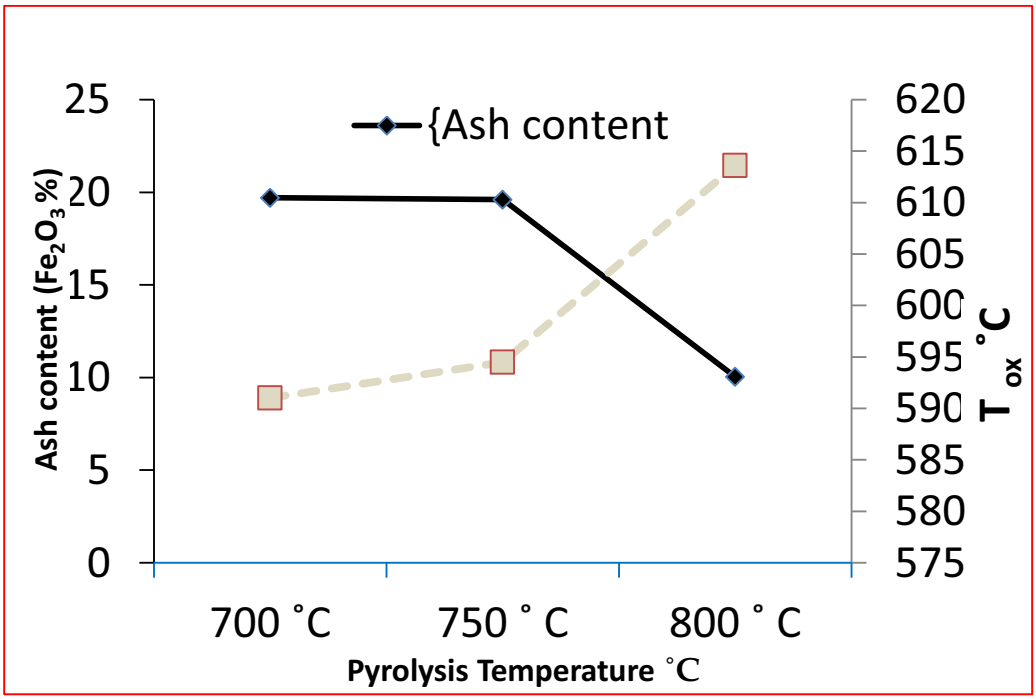

Figure 8. Thermal stability (TOX) and Purity (Ash content) vs. pyrolysis Temperature at 700˚C, 750˚C, and 800˚C

4. Conclusion

In this work, it has been confirmed that the variation of synthesizing temperature has a great influence on the purity and thermal stability of MWCNTs preparation by Injection Chemical Vapor Deposition of Ferrocene/toluene solution 5%Wt over the surface of the quartz tube substrate. Under the studied experimental conditions there where no MWCNTs are formed at the temperatures range from 600 ˚C to 650 ˚C. While carbon microspheres structures are formed in the temperatures range from 850 ˚C to 900 ˚C. The optimum pyrolysis temperature was 700 ˚C which has the lowest (ID/IG) aspect ratio equal to 0.22 recorded by Raman. HRTEM result confirms the high quality of the prepared sample. The high thermal stability of the prepared samples which were observed by TGA indicating that the prepared samples are free of amorphous carbon and consequently have high purity. SEM shows that the average outer diameter increase from 25±6 nm, 50±16 nm to 75±12 nm by increasing the pyrolysis temperature from 700 ˚C, 750 ˚C and 800 ˚C respectively.

5. References

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