Indian Journal of Engineering & Materials Sciences
Vol. 27, December 2020, pp. 1104-1111

Fe-Ni nanoparticle-catalyzed controlled synthesis of multi-walled carbon nanotubes on $CaCO_3$

Srikantaswamy Shivanna[a,b*], Jagadish Krishnegowda[a,c], Abhilash Mavinakere Ramesh[b] & Akshatha Gangadhar[b]

[a]Centre for Materials Science and Technology, Vijnana Bhavan, University of Mysore, Manasagangotri, Mysore, Karnataka 570 006, India.

[b]Department of Studies in Environmental Science, University of Mysore, Manasagangotri, Mysore, Karnataka 570 006, India.

[c]Department of Chemistry, Yuvaraja's College, University of Mysore, Manasagangotri, Mysore, Karnataka 570 005, India.

Received: 25 August 2020

The synthesis of Multi-Walled Carbon Nanotubes (MWCNTs) by Chemical Vapor Deposition (CVD) is becoming most ideal method for producing large quantity of CNT at different temperature conditions. Nano-porous materials such as transition metal carbonates with bimetallic alloy catalyst were used to fabricate MWCNTs with high yield and less amorphous carbon. In the present research work, the MWCNTs were successfully fabricated using Fe-Ni bimetallic catalyst on $CaCO_3$ support with the 180% optimum yield. The proposed yield was high and less-cost effective catalysts to other methods. The yield of MWCNTs depends on four parameters such as growth time (30/45 min), growth temperature (700/730 °C), acetylene flow rate (150/190 ml/min) and argon flow rate (800/900 ml/min). The impact of the reaction temperature and the flow rates were observed to be most significant on the high yield of MWCNTs.

Keywords: Multiwalled carbon nanotube, Chemical vapour deposition, Bimetallic catalyst, Growth mechanism

1 Introduction

Since early 1991, the designing of nanostructured materials such as Carbon nanotubes (CNTs) has attracted enormous attention from the research community because of their potential applications in bio-sensing, wastewater treatment, energy storage, fuel cells and sports materials[1]. CNTs are cylindrical nanostructures with different lengths, diameters and high aspect ratios that account for their extraordinary electrical properties, thermal properties and mechanical strengths[2]. Indeed, CNTs have many interesting and unique properties potentially useful in a variety of biological and biomedical applications[3]. Multi-Walled Carbon Nanotube (MWCNT) have been successfully fabricated by different methods, including laser ablation, Arc discharge, electrolysis, high temperature hydrothermal reaction and chemical vapor deposition[4]. Extensive research efforts have been devoted to the use of laser ablation, arc discharge methods for fabrication of high quality CNTs. However, these methods suffer from many drawbacks, including high operating temperatures, high apparatus costs, and difficulty in scaling-up for marketable purposes. In contrast, the synthesis of MWCNTs via Chemical Vapor Deposition (CVD) remains the most popular, cost effective, flexible, and convenient method of producing high quality and huge quantity MWCNTs at comparatively low synthesis temperatures[2-5]. CVD is the only method that enables us to optimize and fine-tune the structural parameters such as the lengths, diameters, and morphologies of CNTs[6].

In the CVD process, a combination of hydrocarbons (acetylene, methane, carbon monoxide, benzene, ethylene, and toluene) are flown above a metal catalyst (Fe, Co, Ni, Mo, and alloys) placed on a substrate such as alumina, silica, silicon carbide, zeolite, sodium chloride, titania, clays and magnesium oxide among others[7]. The conditions for the catalyst support are optimized to obtain chemical inertness, high surface area, portability, recyclability and low costs of synthesis. Porous and non-porous materials with high surface area (such as SiO_2, Al_2O_3, Zeolites and $CaCO_3$) are an excellent substrate for catalytic CNTs production. Non-porous materials such as $CaCO_3$ reduce the amorphous carbon formation and consequently encourage CNT production. The transition metals, including Fe, Co and Ni and their alloys, have been reported to produce CNTs with high surface areas, catalytic activity and good mechanical

---

*Corresponding author (E-mail: srikantas@hotmail.com)

strength. The growth of CNTs using CVD method has been found to be dependent on various parameters like carbon source, catalyst type, reaction time, and temperature[6-8]. Earlier, Shah and Tali[7] reported that the production of single wall CNTs (SWCNTs) using carbon sources, methane (inert gas) and carbon monoxide. Dai L *et al*. demonstrated[9] that unsaturated hydrocarbons such as acetylene can be used for multi-walled MWCNTs (MWCNT) growth. Chiwaye *et al.*[10] and Liu *et al.*[11]concluded that the carbon source acetylene gas was the most reactive unsaturated hydrocarbon and was most commonly employed for the growth of MWCNTs.

Different support materials such as zeolites[12], silica (SiO_2)[13], alumina (Al_2O_3)[14] and calcium carbonate ($CaCO_3$)[15], have been successfully employed in CVD in conjunction with a metal catalytic for production of CNTs with specific length and diameters (Table 1). This metal catalyst can be a transition metal such as Fe, Co, Mo and Ni, or a bimetallic alloy (Fe-Co, Ni-Fe, and Co-Ni), or a tri-metallic alloy (Fe-Co-Ni, Co-Mo-Fe) catalyst[16]. CNTs production from a bimetallic catalyst supported on a substrate appears to be most promising because of its high catalytic performance and improved CNTs yield. Chiwaye *et al.*[10] and Mhlanga *et al.*[16] have fabricated MWCNTs using Fe-Co catalyst supported on $CaCO_3$, Acetylene as the carbon source and observed presence of CaO in the fabricated MWCNTs.

In the present study, bimetallic Fe-Ni catalyst on $CaCO_3$ support was used as a replacement catalyst for the growth of MWCNTs. Bimetallic catalyst Fe-Ni on $CaCO_3$ support was prepared by using nitrates of iron and nickel with $CaCO_3$. Fe-Ni was selected as a catalyst for MWCNTs growth for its exceptional chemical resistance, its excellent mechanical strength, its high solubility and high rate of carbon diffusion at higher temperatures. Until now, to the knowledge of the author, there has been little or no published information on CVD based synthesis of MWCNTs with 180% yield via bimetallic (Fe-Ni) catalyst supported on $CaCO_3$. In the present study is focused on the preparation of Fe-Ni catalysts supported on $CaCO_3$ using the hydrothermal method for the first time.

2 Methods

Chemicals used in this study include calcium carbonate, nickel nitrate hexahydrate and iron nitrate nonahydrate which were obtained from Sigma Aldrich. All the chemicals used were of analytical grade with purity in the range of 98-99.99%.

In the present experiment, the CVD reactor XD-1200 was used with quartz tube. The quartz tube was placed in a furnace with a heating capacity of about 1200˚C. As shown in Fig. 1, gas cylinders for the carbon source (acetylene) and the carrier gas (argon) were connected to the inlet of the reactor where flow meters were mounted for monitoring the gas flows. The exhaust gases were collected by bubbling in water through an exhaust pump at the reactor outlet.

The synthesis of bimetallic catalyst, Fe-Ni on $CaCO_3$ support was carried out by hydrothermal

Table 1 — Comparison of MWCNT yield from previous and present result .

Catalyst	Precursor and gas mixture (ml/min), Temperature (°C), Duration (min)	Yield (%)	References
Fe-Ni/$CaCO_3$	Acetylene (190) in Argon (800), at 700 °C for 45 min	180	Present work
Co-Ni/SiO_2	Acetylene/nitrogen (220) in Hydrogen (110), at 700°C for 60 min	9.1	Ratkovic *et al.* (2009)[16]
Fe-Ni/SiO_2	Acetylene/nitrogen (220) in Hydrogen (110), at 700°C for 60 min	47.3	Ratkovic *et al.* (2009)[16]
Fe-Co/SiO_2	Acetylene/nitrogen (220) in Hydrogen (110), at 700°C for 60 min	61.8	Ratkovic *et al.* (2009)[16]
Co-Ni/γ-Al_2O_3	Acetylene/nitrogen (220) in Hydrogen (110), at 700°C for 60 min	76.4	Ratkovic *et al.* (2009)[16]
Co-Mo/MgO	Methane (50) in Hydrogen (200), at 950 °C for 40 min	1526	Yardimci *et al.* (2015)[17]
Fe-Co/nano-$CaCO_3$	Acetylene (100) in Nitrogen (300), at 750 °C for 20 min	283	Cheng *et al.* (2006)[18]
Fe-Co/$CaCO_3$ (0.05 mg)	Acetylene (10) in Nitrogen (1167) a, at 720 °C for 30 min	30	Couteau *et al.* (2003)[19]
Fe-Co/$CaCO_3$ (0.5 g)	Acetylene (190) in Argon (230), at 700 °C for 60 min	170	Is' haq, A. M. *et al.*[14]
Fe-Co/$CaCO_3$ (0.5 g)	Acetylene (30) in Nitrogen (300), at 700 °C for 60 min	358	Kathyayini *et al.* (2004)[20]
Fe-Co/$CaCO_3$ (0.2 g)	Acetylene (90) in Nitrogen (240), at 700 °C for 60 min	1215	Mhlanga and Coville (2008); Naseri*et al.* (2010)[15, 21]
Fe-Co/$CaCO_3$ (1.0 g)	Acetylene (90) in Nitrogen (240), at 700 °C for 60 min	250	Motchelaho *et al.* (2011)[22]
Fe-Co/MgO	Acetylene (30) in Nitrogen (300), at 700 °C for 60 min	229	Kathyayini *et al.* (2004)[20]

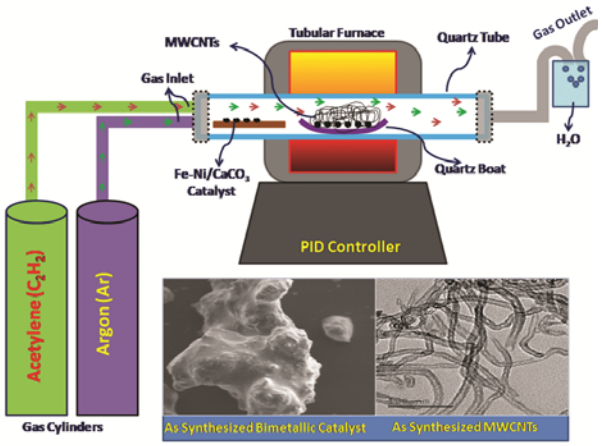

Fig. 1 — Schematic representation of the CVD method used for the synthesis of MWCNTs.

method. Typically 3.62 g and 2.47 g of $Fe(NO_3)_3.9H_2O$ and $Ni(NO_3)_2.6H_2O$ respectively, were weighed and dissolved in 50 cm^3 of distilled water. This was followed by an addition of 10 g of $CaCO_3$ under a continuous stirring condition for 1 h. The 18 ml of resulting solution was transferred into a Teflon liner of 20 ml capacity and fixed with stainless steel autoclave. The autoclave was placed in a hot air oven for duration of 6 hrs, at 180˚C. Later the autoclave was cooled to room temperature and dried at 80˚C for 4hr.

MWCNTs were synthesized by the decomposition reaction of acetylene in a chemical vapor deposition (CVD) reactor. A fixed weight (0.6g) of bimetallic catalyst on a $CaCO_3$ substrate was positioned in the ceramic boat which was then transferred to the interior of the horizontal quartz tube of the CVD furnace. The furnace was then heated at 20˚C/min. The temperature was raised while the argon gas was concurrently released from container and allowed to flow over the catalyst. The initial flow rate of argon gas was kept at 0.5 L/min for purging the air system of the furnace. After 25 minutes, the argon gas flow rate was increased to the required value, i.e. 0.9 L/min at 730˚C and the carbon source acetylene was released to the reaction chamber at the required flow rate of 190 ml/min. The reaction conditions were maintained for 45 minutes to complete the growth of Multi-walled carbon nanotubes. The MWCNTs yield was measured and calculated in percentage using the following formula[24].

$$\text{CNTs yield} = (T_{mass} - C_{mass}) / C_{mass} \text{ X}100 \qquad \ldots (1)$$

where, T_{mass} is the total mass of the final catalyst and MWCNT yield after CVD reaction process, and C_{mass} is the Initial mass of Fe-Ni/$CaCO_3$ catalyst. The fabricated MWCNT were soaked in concentrated acids to remove the residue metals (including Fe, Ni, CaO and $CaCO_3$), the amorphous carbon and impurities. Further the wet MWCNTs residue was oven dried mildly at 110˚C for 15 hours. Finally, the optimal yield of the fabricated MWCNTs and their quality in terms of size, length and morphology were analyzed as a function of the following parameters: Growth temperature, flow rate of argon (carrier gas), flow rate of acetylene (carbon source) and reaction time.

The MWCNTs samples fabricated on the bimetallic/substrate catalyst Fe-Ni/$CaCO_3$ was characterized for its crystallinity using an XRD (XRD-6000 model), thermal stability using a TGA (TGA 4000 model), morphology using a TEM (Tecnai G2 F20-Twin), an field emission scanning electron microscopy (FESEM) as well as Energy-dispersive X-ray spectroscopy (EDX), elements percentage, particle size using dynamic light scattering (DLS) technique (Zetasizer Nano-S series) and BET-surface area using NOVA 4200 model.

3 Results

The bimetallic catalyst shown good catalytic property for the synthesis of MWCNT. The different phases were developed in the synthesis process and it was demonstrated that traces of $NiFe_2O_4$ were found in the catalyst material of CNT growth reaction.

3.1 Acetylene flow rate

Figure 2 explains the flow rate of acetylene between 150 ml/min and 190 ml/min and effect of acetylene on MWCNT yield. The yield of MWCNTs was depending upon the acetylene flow rate. At the flow rate of 190ml/min the yield of MWCNT was high when compare to 190 ml/min of acetylene flow. It was observed that, the yield was irrespective of argon flow rate.

Consider acetylene (C_2H_2) as a source of carbon and the carbon deposition can be calculated using following formula

$$Yc = (100 \text{ x } m_f) / m_s \qquad \ldots (2)$$

Where, Yc = Yield of CNT, m_f = mass of purified CNT and m_s= mass of carbon in the C_2H_2, which can be calculated by using Equation (3);

$$m_s(\text{g}) = [\text{Flow rate (l/min)} \times \text{Time(min)}/22.4(\text{l/mol})] \times 24(\text{g/mol}) \quad \ldots (3)$$

Table 2 shows the different acetylene flow rates vs carbon deposition and it can be observed that, the increased flow rate of acetylene increased the carbon weight, because it is helpful for the high yield of MWCNT. Besides the yield of MWCNT have decreased at 900 ml/min argon flow rate, because of the acetylene to argon ratio. The CNT yield has been depending on acetylene flow rate which is justified theoretically as shown in the Table 3.

Table 2 — Effects of different parameters such as time, temperature, argon and acetylene flow rate with MWCNT yield.

Run	Time (min)	Temperature (°C)	Argon flow (ml/min)	Acetylene flow rate (ml/min)	MWCNT yield (%)
1	30	700	800	150	110
2	30	700	800	190	165
3	30	700	900	150	130
4	30	700	900	190	158
5	30	730	800	150	75
6	30	730	800	190	80
7	30	730	900	150	40
8	30	730	900	190	120
9	45	700	800	150	132
10	45	700	800	190	180
11	45	700	900	150	135
12	45	700	900	190	145
13	45	730	800	150	48
14	45	730	800	190	60
15	45	730	900	150	66
16	45	730	900	190	42

3.2 Argon flow rate

Argon gas was considered as the carrier gas which have major role in the production of MWCNT. Figure 3 shows that the flow rate of Argon gas which was tuned between 800 ml/min and 900 ml/min and its effects on the yield of MWCNT. Figure 3a shows that the different argon flow rate at acetylene

Table 3 — Theoretical justification of acetylene flow rate on CNT yield.

S. No.	Acetylene flow rate (ml/min)	Reaction time (min)	C available for deposition (g)
1	150	30	4.8214
2	150	45	7.232
3	190	30	6.1071
4	190	45	9.1607

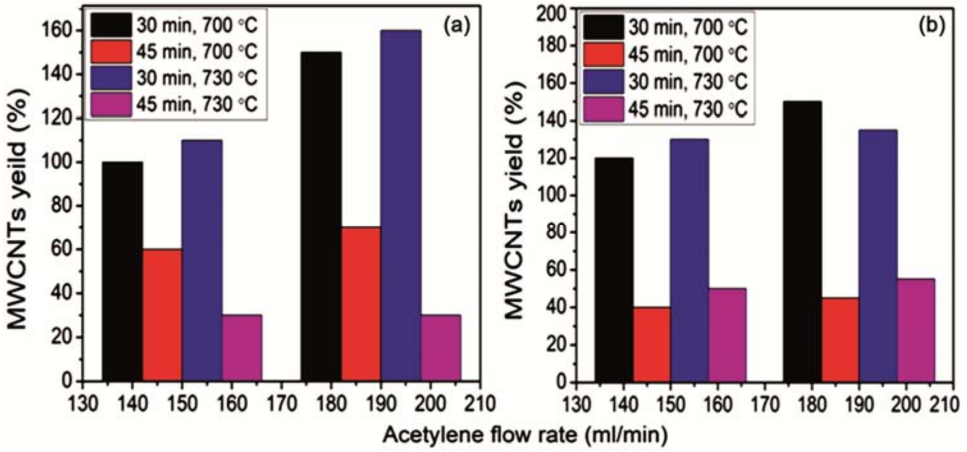

Fig. 2 — Effect of acetylene flow rate on MWCNT yield at Argon flow rate of (a) 800 ml/min and (b) 900 ml/min.

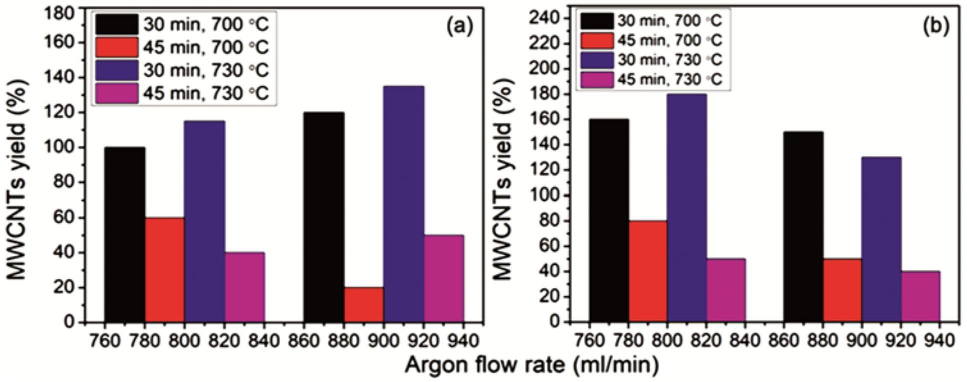

Fig. 3 — Effects of argon flow rate on MWCNT yield at acetylene flow rate (a) 150 ml/min and (b) 190 ml/min.

flow rate 150 ml/min and Fig. 3b shows that the different argon flow rate at acetylene flow rate 190 ml/min. It was indicated that the yield of MWCNT was increased at the argon flow rate 900ml/min at 730°C with duration of 30 minutes which shown in Fig. 3a and yield of MWCNT was increased at the argon flow rate 800ml/min at 730°C with the duration of 30 minutes which shown in Fig. 3b. Argon was behaved differently with the connection between acetylene and catalyst[25], hence, the high amount of argon gas have been decreased. Therefore it was considered that the growth reaction mechanism was balanced between acetylene and argon gases[26].

3.3 Morphology

All the published literature indicates that, the MWCNTs synthesis always associate with small quantity of impurities in all type of technique methods. The common impurities are amorphous carbon, fullerenes and different metals (typically Fe, Co, Mo or Ni) that were introduced as catalysts during the synthesis. The above said impurities were able to damage the morphology of MWCNTs, therefore it is very necessary to remove these impurities before analysis by acid purification technique to obtain pure MWCNTs but, no purification method that fulfills all the requirements for technical processing is currently available[27]. In this study, the as-synthesized MWCNTs were purified using 100 ml of 30% H_2SO_4 per 1 g of MWCNTs sample[23]. In order to compare the purity of the MWCNTs, experimental runs 2, 4 and 10 were selected and the FESEM images were shown in Fig. 4. As synthesized MWCNTs were purified by treatment with sulphuric acid, but in the present research work the presence of $CaCO_3$ formed as $CaSO_4$ precipitate which was removed by decantation method to obtain pure MWCNTs.

Figure 4 shows FESEM images of MWCNTs synthesized by CVD method and it was observed that the different impurities like amorphous carbon, metal particles were present on the surface of MWCNTs. The diameter of the MWCNTs produced were 55 nm with the presence of an encapsulated catalyst. After purification, there was a partial disappearance of the black spot and a decrease in the diameter to 48 nm and it was evident from our published article Srikantaswamy *et al.*[28] and Moreno *et al.*[29].

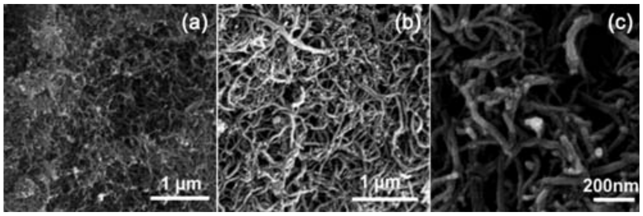

Fig. 4 — FESEM images of as-synthesized from (a) run 2, (b) run 4 and (c) run 10 MWCNT.

The MWCNTs in experimental runs 2 and 4 contain excessive amount of amorphous carbon when compared to those in run 10. It was observed by FESEM image that the metal Fe, $CaCO_3$ and CaO were present in the sample with small quantity. The results from EDX it was evident that the carbon contents in the purified and as-synthesized MWCNTs were sufficiently high, ranging from 80 to 98.55%.

The compositions of the as-synthesized samples examined were shown the presence of $CaCO_3$, CaO, and oxides of Fe metal in the samples. However, it is important to note that the carbon contents in the purified and as-synthesized MWCNTs were sufficiently high, ranging from 80 to 98.55%. Further, the results of a FESEM analysis, as shown in Fig. 4 revealed that, MWCNTs were partially modified during the H_2SO_4 acid treatment.

The TEM analysis of as synthesized MWCNTs was presented in Fig. 5. The morphology of MWCNTs were observed unevenly in diameters and found that the few metal nanoparticles encapsulated in the interior of nanotube sample (Fig. 5a). According to the results FESEM and EDS analysis, the metal particles are not removed from MWCNTs even after acid purification process. The SAED patterns of samples, as shown in Fig. 5d, explains the graphitic (002) properties as synthesized MWCNTs and also it is matched with Raman spectra (Fig. 6c).

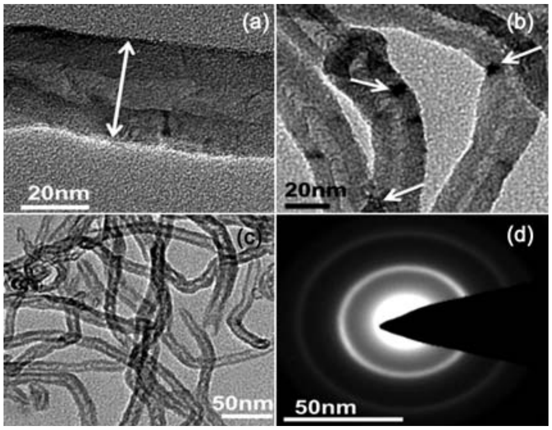

Fig. 5 — TEM images of run 10 MWCNTs (a) with multiple walls, (b) active sites having metal nanoparticles on the support, (c) dispersed MWCNT and (d) SAED pattern.

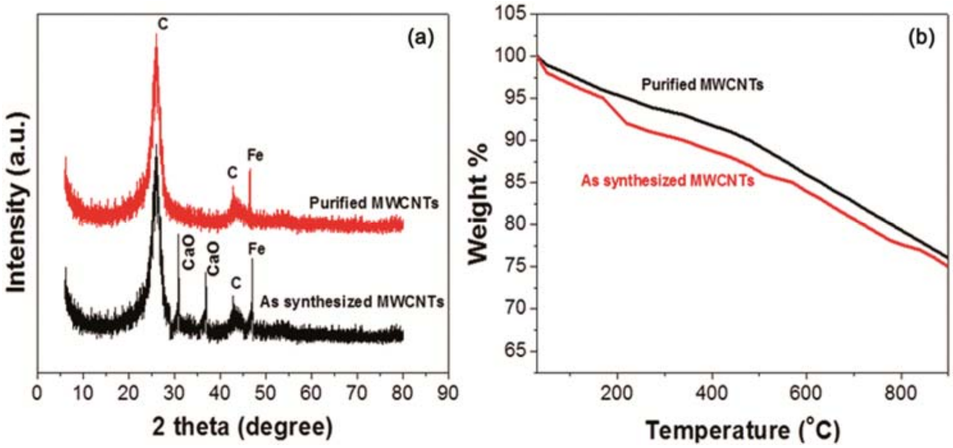

Fig. 6 — (a) XRD spectra and (b) TGA curve of purified and as synthesized MWCNTs of purified MWCNTs.

X-Ray diffraction technique was used to investigate the crystallinity of the purified and as-synthesized MWCNTs. The XRD spectra shown in Fig. 6(a), reveals the characteristic pattern of graphitized carbon and also the (002) graphitic line observed around 26°. This pattern also reveals a high degree of crystallinity, suggesting a low content of amorphous carbon and impurities present in the catalyst and also other peaks attributable to the graphitic planes of carbon have occurred at 2θ and 44°. In order to use the X-ray diffraction technique for investigating phases that are present before and after acid purification, XRD patterns of the purified MWCNTs with the highest and the lowest yields were collected. During purification process the impurities like CaO and $CaCO_3$ were removed but the iron was not removed and it was present in the form of iron carbide (Fe_3C).

The thermo gravimetric analyses of purified MWCNTs were carried out at heating rate of 10°C/min up to 900°C in the condition of nitrogen gas. Figure 6b explained the curve of % weight loss of MWCNTs against temperature. It was observed that the purified MWCNTs start to degrade around 100°C which was responsible for the loss of water molecules. In addition, the weight loss at 200°C was responsible for the loss of amorphous carbon. The weight loss at 540°C was responsible for the loss of metal ferrite molecules and weight loss at 720°C was responsible for the loss of metal oxide molecules.

4 Discussion

Experimental runs 10 and 2 were used to study the effect of synthesis time on morphology of the MWCNTs produced by CVD. The same growth parameters (i.e. 700°C temperature, 190 ml/min Acetylene flow rate and 800 ml/min argon flow rate) were used to grow both MWCNTs samples, but at different growth duration. Sample 10 was obtained at 45min. duration while sample 2 was obtained at 30min. duration. As revealed by the FESEM images (Figs 4b and 4c), the effects of growth time on MWCNTs morphology tends to affect the aspect ratio and the tube density. Kara *et al.*, explains the effects of different parameters like flow rate of carrier gas on CVD for the growth of MWCNTs which is also agrees for the present research work. Further Mhlanga *et al.*, demonstrate that the high aspect ratio of MWCNTs obtained due to smaller reaction times when compare to longer time. In the present research, it was found that the experimental run 2 of duration 30 Minutes shows high aspect ratio when compare to experimental run 10 of duration 45 Minutes.

The CNT growth mechanisms can be understand based on the reaction conditions and the post-deposition product analysis. Several groups have proposed several possibilities; many of them are contradicting and so far, there is no single MWCNTs growth mechanism have not been well established. Acetylene gas split into hydrogen and carbon reacts with bimetallic catalyst to deposit as carbon, while hydrogen gas was escaped. Formation of carbon precipitate will occurred with crystalline structure to obtain tube like structure in nanosize. In the present work, the interaction between catalyst and substrate was strong, the MWCNTs were developed on top of catalyst and catalyst remains in the bottom. Therefore, the present research work on the MWCNTs was developed based on base growth model. This mechanism explains the good interaction between bimetallic catalyst (Fe-Ni) and substrate ($CaCO_3$) for the precipitation of MWCNTs.

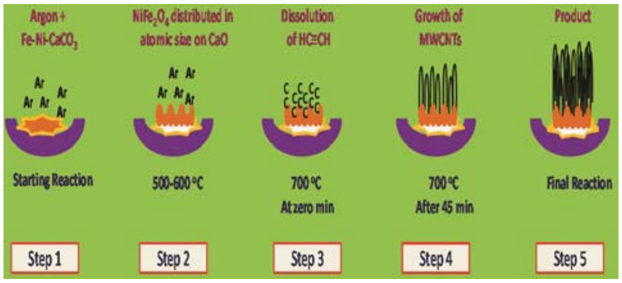

Fig. 7 — Mechanism of MWCNTs fabrication in CVD process.

The mechanism of CVD synthesis of MWCNTs has been explained in Fig. 7. In step 1, the CVD reaction was started by placing the bimetallic (Fe-Ni) catalyst on $CaCO_3$ support on quartz boat, controlled argon gas was flowed inside of quartz tubular furnace. At the temperature between 500 to 600^{o}C, the bimetallic catalyst in the form of $NiFe_2O_4$ make its surface available for the deposition of hydrocarbons like acetylene gas as shown in step 2. The deposited acetylene on bimetallic surface decomposed to form C and H elements at 700^{o}C, hydrogen flies away and carbon dissolution has taken place on the bimetallic surface as shown in step 3. The dissolution of carbon continued for 45 minutes at the temperature 700˚C, the growth of MWCNTs were observed in step 4, when the catalyst surface was covered by MWCNTs, further growth was stopped because of the unavailability of the catalyst surface. However, the MWCNTs with high yield were developed on the surface of the catalyst with some metal nanoparticles incorporated in the hollow cavity of MWCNT, which has become a challenging task in the purification. Growth mechanisms upto step 3 are known process and step 4 and 5 are being used in the present work. Step 5 was the illustration of the final product obtained by CVD process which contains as grown MWCNTs with 180% yield and metal atoms in the form of Fe_3C, which is subsequently removed by purification process as explained earlier.

5 Conclusions

The present study investigated the combined influences of key processes and parameters on the yield and quality of MWCNTs using hydrothermally synthesized with bimetallic catalyst. The results of our investigation are summarized such as, MWCNTs were successfully fabricated using the synthesized Fe-Ni/$CaCO_3$ catalyst with optimum yield of 180% in the experimental conditions of 45 minutes of MWCNT growth at 700^{o}C, 190 ml/ min Acetylene flow rate, and 800 ml/min argon flow rate. The impact of the reaction temperatures and the flow rate of acetylene were observed to be the most significant on the yield of MWCNTs. The proposed MWCNT have reached a yield of 180%, as opposed to lower yields from other catalysts. During the MWCNTs growth, the four parameters such as temperature, time, argon flow rate and acetylene flow rate, were found to have effects on morphology of the MWCNTs. Temperature and the acetylene flow rate have mainly affected the diameters of the MWCNTs, whilst the growth time and the argon flow rate have primarily affected the aspect ratios. Purification of MWCNTs results small quantities of $CaSO_4$ precipitate which was removed by decantation method to obtain pure MWCNTs.

Acknowledgment

The authors are very thankful to the University Grant Commission (UGC) and University of Mysore for the financial support by granting project "University with Potential for Excellence" (UPE) and "Center with Potential for Excellence in Particular Area" (CPEPA).

References

1 Iijima S, *Nature, 354* (1991) 56.
2 Yang X, Zou T, Shi C, Liu E, He C & Zhao N, *Mater Sci Eng, 660* (2016) 11.
3 Lin Y, Taylor S, Li H, Fernando K S, Qu L, Wang W, Gu L, Zhou B & Sun YP, *J Mater Chem, 14* (4) (2004) 527.
4 Hutchison J, Kiselev N, Krinichnaya E, Krestinin A, Loutfy R, Morawsky A, Muradyan V, Obraztsova E, Sloan J & Terekhov S, *Carbon, 39* (5) (2001) 761.
5 Tombros N, Buit L, Arfaoui I, Tsoufis T, Gournis D, Trikalitis PN, van der Molen S J, Rudolf P & van Wees B J, *Nano lett*, *8* (9) (2008) 3060.
6 Maccallini E, Tsoufis T, Policicchio A, La Rosa S, Caruso T, Chiarello G, Colavita E, Formoso V, Gournis D & Agostino R G, *Carbon, 48* (12) (2010) 3434.
7 Shah KA & Tali B A, *Mater Sci Semicond Process, 41* (2016) 67.
8 Tsoufis T, Jankovic L, Gournis D, Trikalitis P N & Bakas T, *Mater Sci Eng B, 152* (1-3) (2008) 44.
9 Dai L, Patil A, Gong X, Guo Z, Liu L, Liu Y & Zhu D, *Chem Phys Chem, 4* (11) (2003) 1150.
10 Chiwaye N, Jewell L, Billing D, Naidoo D, Ncube M & Coville N, *Mater Res Bull,56* (2014) 98.
11 Liu WW, Chai SP, Mohamed AR & Hashim U, *J Ind Eng Chem, 20* (4) (2014) 1171.
12 Liu J, Jiang Z, Yu H & Tang T, *Polym Degrad Stabil*, *96* (10) (2011) 1711.
13 Wang Y, Wei F, Gu G & Yu H, *Physica B Condensed Matter*, *323* (1-4) (2002) 327.

14 Jeong S W, Son S Y & Lee D H, *Adv Powder Technol, 21* (2) (2010) 93.

15 Is'haq, A M, Bankole M T, Abdulkareem A S, Ochigbo S S, Afolabi A S & Abubakre O K, *S Afr J Chem Eng, 24* (2017) 17.

16 Mhlanga S D & Coville N J, *Diam Relat Mater, 17* (7-10) (2008) 1489.

17 Ratkovic S, Kiss E & Bošković G, *Chem Ind Chem Eng Q, 15* (4) (2009) 263.

18 Yardimci A I, Yılmaz S & Selamet Y, *Diam Relat Mater, 60* (2015) 81.

19 Cheng J, Zhang X, Luo Z, Liu F, Ye Y, Yin W, Liu W & Han Y, *Mater Chem Phys, 95* (1) (2006) 5.

20 Couteau E, Hernadi K, Seo J W, Thien-Nga L, Miko C, Gaal R & Forro L, *Chem Phys Lett, 378* (1-2) (2003) 9.

21 Kathyayini H, Nagaraju N, Fonseca A & Nagy J, *J Mol Catal A Chem, 223* (1-2) (2004) 129.

22 Naseri M G, Saion E B, Ahangar H A, Shaari A H & Hashim M, *J Nanomater,* (2010) 75.

23 Motchelaho M A, Xiong H, Moyo M, Jewell L L & Coville N J, *J Mol Catal A Chem*, *335* (1-2) (2011) 189.

24 Taleshi F, *Int Nano Lett, 2* (1) (2012) 23.

25 Khorrami S & Lotfi R, *J Saudi Chem Soc, 20* (4) (2016) 432.

26 Yap Y K, Kayastha V, Hackney S, Dimovski S & Gogotsi Y, *Mater Res Soc Symp Proc, (2004)* 818.

27 Kaatz F H, Siegal M, Overmyer D, Provencio P & Tallant D, *Appl Phys Lett, 89* (24) (2006) 241915.

28 Swamy S S, Calderon Moreno J M & Yoshimura M, *J Mater Res, 17* (4) (2002) 734.

29 Moreno J M C, Swamy S S, Fujino T & Yoshimura M, *Chem Phys Lett, 329* (3-4) (2000) 317.