



Effect of chemical vapor deposition parameters on the diameter of multi-walled carbon nanotubes

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Abstract

The multi-walled carbon nanotubes (MWCNTs) with controlled diameter distribution are useful in the fabrication of composite materials as reinforcement, due to their superior strength and toughness. Chemical vapor deposition (CVD) is a viable process to synthesize MWCNTs. In this investigation, an attempt has been made to study the effect of CVD process parameters (reaction temperature, flow rate of precursor gas, process time) on the mean diameter of MWCNTs. The MWCNTs of controlled diameter distribution was selectively grown on NiO catalyst supported by Al₂O₃ nano particles. The argon and acetylene were used as carrier and carbon precursor gas, respectively. The catalyst and carbon samples were characterized using field emission scanning electron microscopy, high-resolution transmission electron microscopy, Raman spectroscopy and thermogravimetric/differential thermal analysis. From this investigation, it is understood that the increase in reaction temperature and flow rate of precursor gas increased the mean diameter of MWCNTs but increase in process time decreased the diameter. The diameter distribution and quality of MWCNTs are strongly influenced by the diameter of the catalyst particles.

Keywords Nanotechnology · Carbon nanotubes · Chemical vapor deposition · Mean diameter

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Introduction

The significance of carbon nanotubes (CNTs) in the field of nanotechnology was noticed abundantly by the researchers, after the tubular needle growth model, proposed by the Ijima in 1991 [1]. The growth model of CNTs was proposed to be, the rolling up graphene-hexagon sheet into a cylinder shape to form a tubular structure. The CNTs growth model possess the similar way of the bacon's scroll model [1]. CNTs are costly and highly demanded nanomaterial around the world, due to their excellent electrical conductivity [2], tensile strength [3] and thermal conductivity. An elastic modulus of multi-walled carbon nanotubes (MWCNTs) is tenfold higher than the any commercial, industrial fiber [4].

To use CNTs in many applications, it is indeed to produce these nanomaterials with highly precise structure and in large scale at an affordable cost. The CNTs were synthesized by various methods, mainly: arc discharge [5], laser ablation [6] and chemical vapor deposition (CVD) [7, 8]. As compared to other methods, CVD is a simple and economical technique for the growth of CNTs at low temperature and ambient pressure [9]. The required structure and



morphology of CNTs were achieved by a set of controlled variables [10, 11].

Nickel oxide (NiO) was specifically selected as the catalyst material, due to its strong interaction with the outer graphitic plane of CNTs than some other metal oxide catalyst like copper (Cu) [12–14]. NiO is supported by alumina (Al_2O_3) because of its higher activity and its support to the metal catalyst in higher temperature for the growth of MWCNTs [15]. Acetylene gas seems to be favoring the growth of CNTs since it contains smaller carbon atoms [16].

CVD process parameters were varied to control the growth of CNTs, such as effect of precursor gas flow rate [17], carrier gas flow rate [18], process time [19], and reaction temperature [20]. Besides, only few researchers have investigated on the growth of CNTs by CVD process. No systematic study has been reported so far to quantitatively assess the effect of CVD parameters on mean diameter of MWCNTs. Therefore, this investigation was taken up to study the effect of CVD parameters such as reaction temperature, flow rate of precursor gas and reaction time on the mean diameter of MWCNTs.

Experimental

To achieve the desired objective, the present investigation was planned in the following sequence.

- (i) Identify the important CVD process parameters and their feasible working limits
- (ii) Prepare the suitable catalyst
- (iii) Synthesize CNTs by CVD process
- (iv) Purify CNTs by wet chemistry and filtering methods

- (v) Characterize MWCNTs by FESEM, HRTEM, TGA/DTA, and Raman spectroscopy analysis
- (vi) Analyze the results to optimize appropriate CVD process parameters to obtain MWCNTs with equal diameter distribution with defectless structure

Identify the important CVD process parameters and their limits

From the literature [21–24] review, the predominant CVD parameters which control the morphology and diameter of MWCNTs were identified. They are (a) reaction temperature (b) flow rate of precursor gas (c) process time. Trial experiments were conducted initially and NiO was used as the transition metal catalyst and it was supported by Al_2O_3 . Ten milligrams of catalyst was loaded into the CVD chamber and it was maintained constant for all the experiments. The morphology of the NiO/ Al_2O_3 catalyst was spherical in shape (Fig. 1a). From the trial experiments, the following observations were made:

- (i) If the reaction temperature was below 700 °C, the growth of CNTs was affected due to the lesser active sites on the surface area of the catalyst. If the reaction temperature was greater than 1000 °C, the deposition of amorphous carbon and disoriented CNTs were observed, due to self-diffusion of acetylene towards the catalyst and also the over agglomeration of catalyst particles.
- (ii) If the precursor gas flow rate was less than 100 ml min⁻¹, there was no tubular morphology in the samples, due to insufficient diffusion of carbon atoms to the catalyst particles. If the precursor flow rate was more than 180 ml min⁻¹, the highest number of tubular CNTs were found, but the amorphous

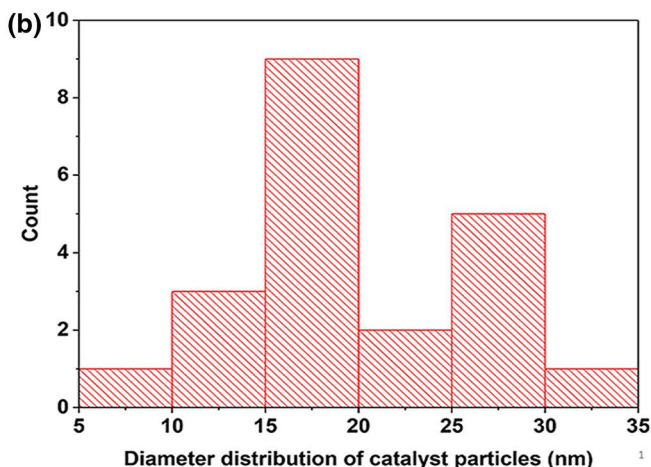
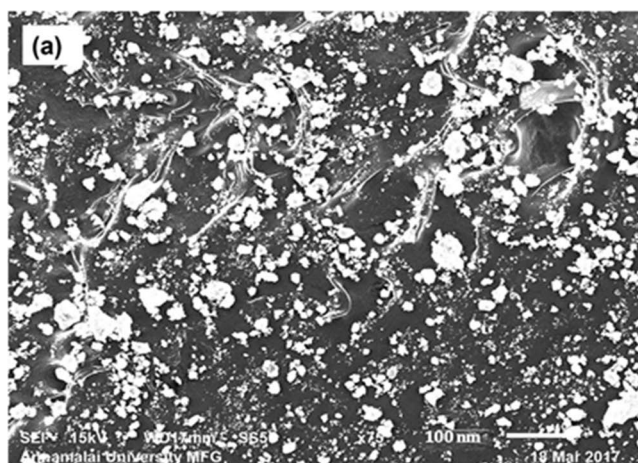


Fig. 1 a Morphology of NiO/ Al_2O_3 powder catalyst, b NiO/ Al_2O_3 particle size distribution

Table 1 Some worldwide databases in the area of neuroinformatics

S.no	Parameters	Unit	Level		
			Minimum	Medium	Maximum
1	Temperature	°C	800	900	1000
2	Flow rate of precursor gas	ml min ⁻¹	100	140	180
3	Process time	min	15	25	35

carbon inclusions in the sample were equal to the well-aligned CNTs.

- (iii) If the process time was less than 15 min, the defect was found in the outer ring of CNTs due to insufficient reaction time. If the process time was more than 35 min, amorphous carbon and defective structure were found.

It was very difficult to study the effect of CVD process parameters on the diameter distribution of CNTs if misaligned CNTs were found in larger number. Hence, the above points were discussed to fix the working limit that decides the good surface morphology of CNTs.

All the above-listed limitations and conditions were considered and the feasible working limits were selected to conduct the experiments without any difficulties to attain the desired objective. The working range of CVD parameters employed in this investigation is presented in Table 1.

Catalyst Preparation

The NiO/Al₂O₃ catalyst was prepared by impregnating 1 g of fumed alumina nanoparticles with 0.245 g of Ni (NO₃)₆H₂O in 30 ml of methanol solution. The impregnation typically lasted for 1 h at room temperature using a magnetic stirrer. The methanol solution was removed via rotary evaporator and obtained material was then heated at 150 °C overnight followed by grinding into a fine powder. This resulting product, [11, 25] denoted as NiO/Al was used as a catalyst in this investigation.

Synthesize MWCNTs

The MWCNTs were synthesized at atmospheric pressure in a quartz tube reactor (diameter: 70 mm, length: 300 mm) by thermal chemical vapor deposition machine. The synthesis of MWCNTs was carried out as per the conditions prescribed by the Table 1.

In these experimental conditions, the catalyst loading (10 mg) and carrier gas (Argon: 100 ml min⁻¹) flow rate were kept constant. The catalyst was loaded into the center

of the hot zone reactor and then argon gas was supplied (100 ml min⁻¹) until the attainment of required reaction temperature. Then argon was stopped and the carbon precursor gas (acetylene) was supplied to the reaction zone according to the process time. Later acetylene was replaced with argon until the furnace reaches room temperature. The carbon samples along with catalyst particles were collected from the quartz tube for the purification process to remove amorphous carbon and catalyst particles [11].

Purify MWCNTs

After the CVD process, the samples were purified by three steps (a) acid treatment (b) sonication and (c) filtered in sintering ceramic crucible. In the acid treatment step, the samples (derived from CVD process) were stirred in concentrated nitric acid for 3 h at room temperature. During this process of acid treatment carbon diffused samples, metal content was dissolved in the acid, but CNTs withstood the strong acid attack. After acid treatment, the metals (Catalysts particle) and amorphous carbon products were dissolved in acid solution due to the acid attack. The crystalline carbon products were free from catalyst [26–28] materials. The crystalline carbon samples were suspended in ethanol solution and sonicated for 10 min. In this process, the agglomerated particles separated and MWCNTs were filtered in sintering ceramic crucible and carbon products were dried in a furnace.

Characterize MWCNTs

The MWCNTs synthesized by the CVD process were characterized by the field emission scanning electron microscopy (FESEM) technique. The FESEM analysis was carried out to confirm the presence of a tubular structure in the carbon samples. Further, carbon samples were analyzed by high-resolution transmission electron microscopy (HRTEM) technique, to examine the number of walls present in MWCNTs and its structure. The diameter distribution of MWCNTs was measured by Image J analysis software. The MWCNTs were analyzed by Raman spectroscopy, to reveal the presence of G and D band in the corresponding spectra, mainly to infer structural information about the tubes [29]. Further, the MWCNTs were subjected to TGA/DTA analysis to find the thermal stability and purity of tubes. The MWCNTs samples were subjected to image and analytical techniques, to obtain optimized CVD parameters and to study their effect on structure, stability, and diameter of MWCNTs.



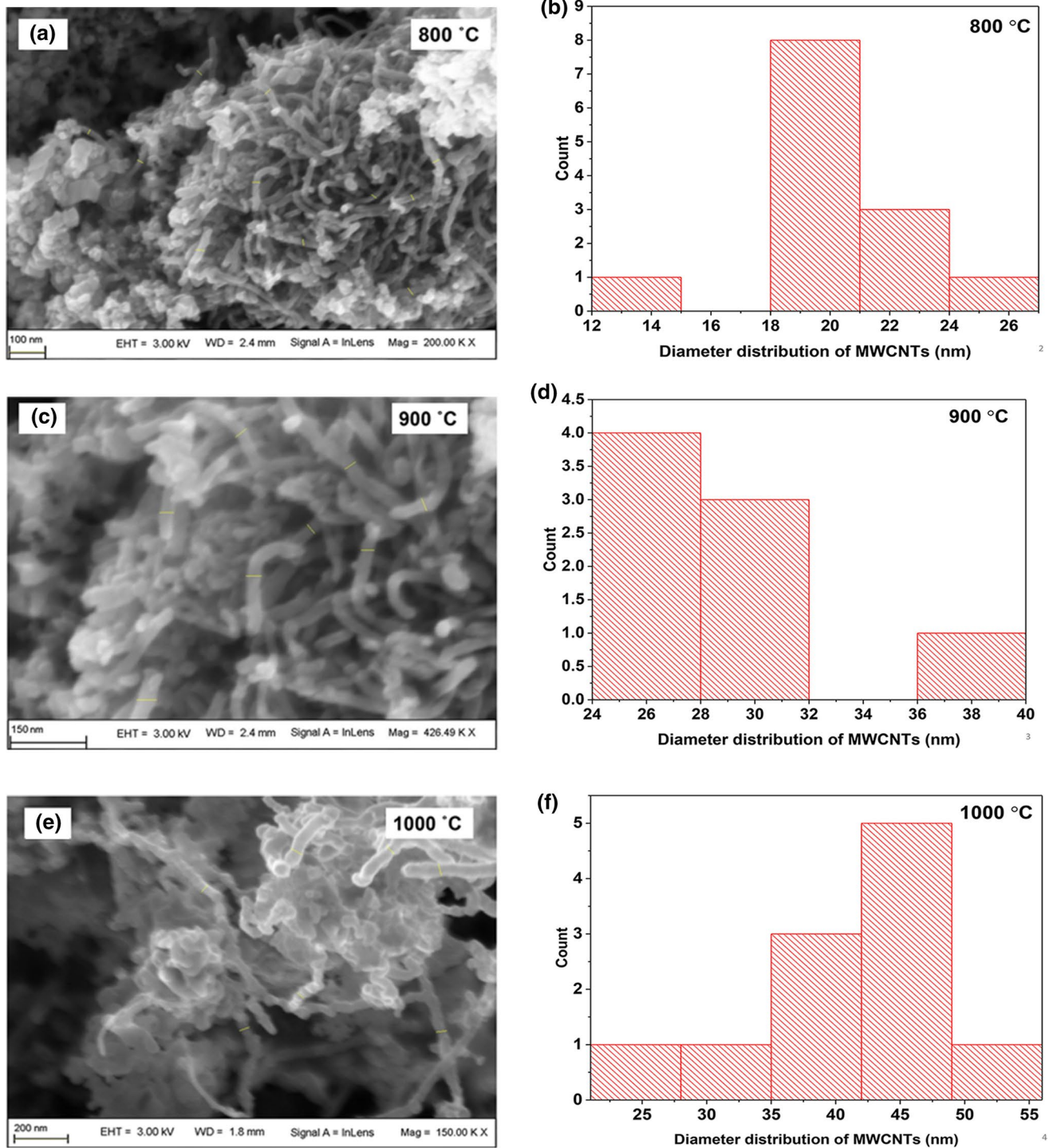


Fig. 2 FESEM image of MWCNTs grown at different reaction temperatures (a, c, e) and distribution of MWCNTs diameter as a function of reaction temperature (b, d, f)

Results and discussion

Characterization of NiO/Al catalyst

For the controlled growth of CNTs, the size of the catalyst particles should be taken into consideration. The catalyst initiates the growth of CNTs and tube diameter governed by the size of the catalyst particle [30]. The Fig. 1a, b shows the NiO/Al₂O₃ pristine structure, morphology and particle size distribution. The NiO/Al₂O₃ catalyst particles have sphere-shaped morphology and the particle size distribution ranges from 15 to 30 nm approximately. The particles are in circular shape and some catalyst particles are agglomerated even before the start of the experiment. So numerous factors may affect the diameter and distribution of CNTs.

Effect of reaction temperature

To study the effect of reaction temperature, it was varied from 800 °C to 1000 °C in steps of 100 °C but the precursor flow rate and process time were kept constant at 140 ml min⁻¹ and 25 min, respectively. The morphology of MWCNTs observed under FESEM and the diameter distribution of MWCNTs are depicted in Fig. 2.

The growth of MWCNTs at different reaction temperature shows the twisted and entangled tubular structure. At reaction temperature 800 °C, the MWCNTs diameter distribution ranges from 15 to 28 nm, at 900 °C MWCNTs diameter ranges from 25 to 40 nm and at 1000 °C diameter ranges from 28 to 53 nm. From Fig. 2, it could be inferred that the reaction temperature is showing a directly proportional relationship with the mean diameter of the MWCNTs. The Fig. 3 shows the effect of reaction temperature on the mean diameter of MWCNTs. The enlargement of mean diameter of MWCNTs at higher temperatures is due to the sintering effect of catalyst particles results in small catalyst particle agglomerates to form larger particles [31].

The MWCNTs diameter distribution (15–24 nm) at reaction temperature 800 °C is relatively depended on the catalyst particles diameter distribution (15–30 nm) and it is clearly evident in Fig. 2a. The MWCNTs diameter distribution (22–32 nm) at 900 °C is quite higher compared to the catalyst particles distribution. Therefore, the agglomeration of catalyst particles starts from the reaction temperature above 800 °C. It is understood that the increase in reaction temperature tends to increase the reduction temperature [32]; this reduction effect causes the catalyst particles to agglomerate and agglomerated particles result in a growth of larger diameter MWCNTs.

Effect of the flow rate of the precursor gas

To study the effect of precursor gas flow rate, it was varied from 100 to 180 ml min⁻¹ in steps of 40 ml min⁻¹ but the reaction temperature and process time were kept constant at 900 °C and 25 min, respectively. The morphology of MWCNTs observed under FESEM and the diameter distribution of MWCNTs are depicted in Fig. 4. The MWCNTs growth at a higher flow rate of precursor gas shows the deposition of amorphous carbon on the sidewalls of CNTs. At flow rate of precursor gas 100 ml min⁻¹, the MWCNTs diameter distribution ranges from 14 to 22 nm; at 140 ml min⁻¹, from 25 to 40 nm; and at 180 ml min⁻¹, from 25 to 52 nm. From Fig. 4, it could be inferred that the flow rate of precursor gas is showing a directly proportional relationship with the mean diameter of the MWCNTs. Fig. 5 shows the effect of precursor flow rate on the mean diameter of MWCNTs.

The diffusion of carbon atoms towards the catalyst particles was low, at a low flow rate of acetylene gas [17]. The lack of diffusion retracts the dispersion of carbon atoms in the catalyst particles leading to decrease in diameter distribution of MWCNTs clearly evident in Fig. 4a. If the flow rate of acetylene gas is high, the diffusion of large amounts of carbon atoms towards the catalyst particle was high that tends to increase the dispersion rate. At high diffusion rate of carbon, the large amount carbon present in catalyst particle starts to reduce the activity of the catalyst, due to catalyst particles being covered by amorphous carbon, that increase the thickness of the MWCNTs [33] and it is clearly evident in Fig. 4e.

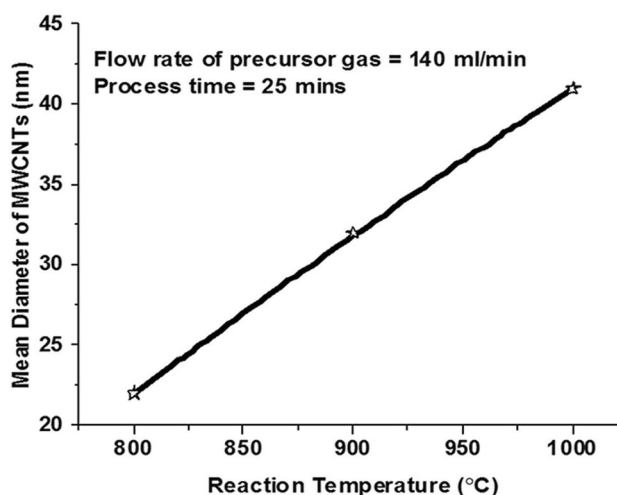


Fig. 3 Effect of reaction temperature on the mean diameter of MWCNTs

Effect of process time

To study the effect of process time, it was varied from 15 min to 35 min in steps of 10 min but the reaction temperature and flow rate of precursor gas were kept constant at 900 °C and

140 ml min⁻¹, respectively. The morphology of MWCNTs observed under FESEM and the diameter distribution of MWCNTs are depicted in Fig. 6. The MWCNTs' growth at different processing time shows the bundles and well-aligned carbon structures. At a process time of 15 min, the diameter

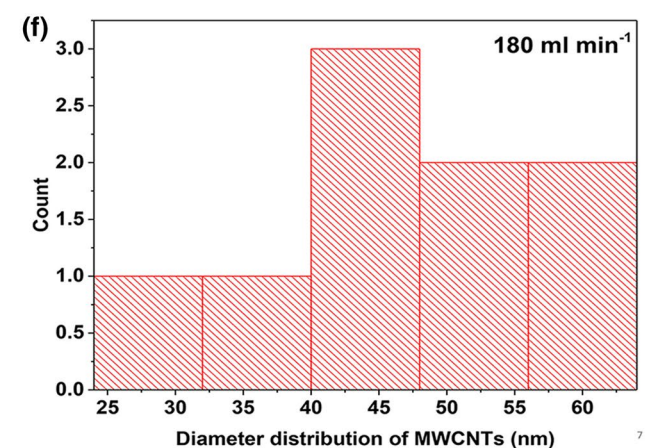
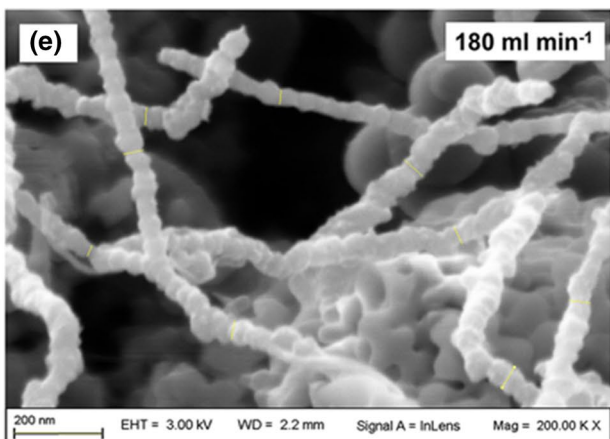
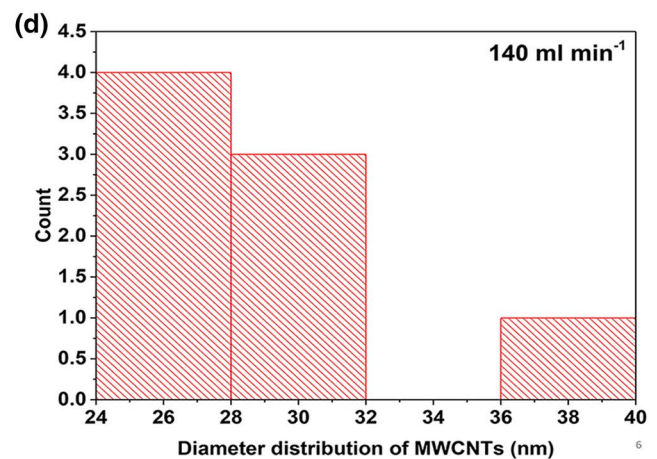
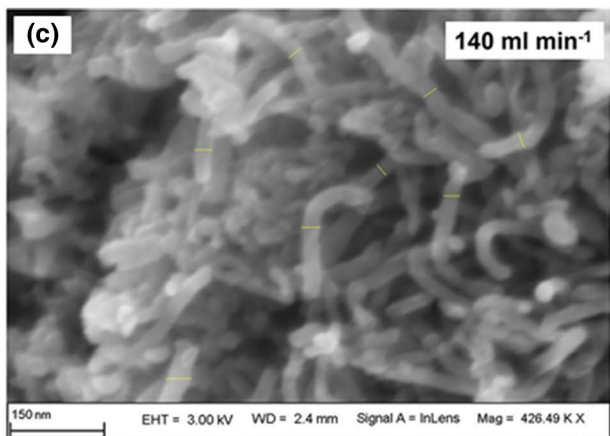
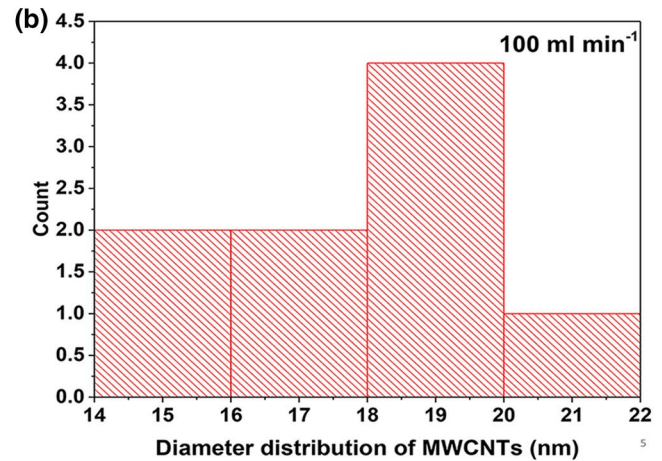
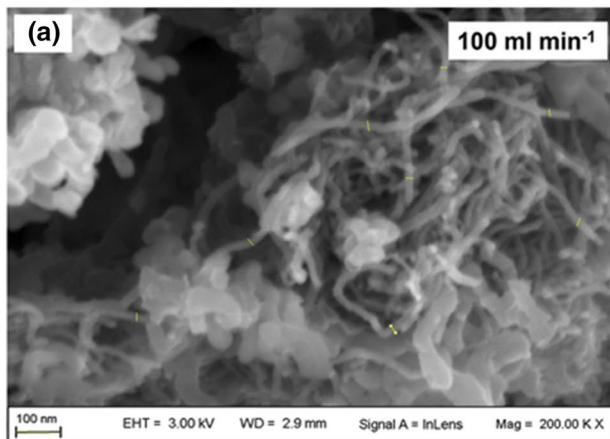


Fig. 4 FESEM image of MWCNTs grown at different flow rate of precursor gas (a, c, e) and distribution of MWCNTs diameter as a function of flow rate of precursor gas (b, d, f)

of MWCNTs ranges from 20 nm to 50 nm, at the process time of 25 min, the diameter ranges from 25 to 40 nm and at process time of 35 min, the diameter ranges from 10 to 30 nm. From Fig. 6, it could be inferred that the process time is showing the inversely proportional relationship with the mean diameter of the MWCNTs. Fig. 7 shows the effect of process time on the mean diameter of MWCNTs.

The mean diameter of the MWCNTs decreases, when processing time increases. This effect can be explained by two hypotheses,

- (i) Nagaraju et al. [15] reported that higher reaction time favors better results in acetylene-to-nanotube conversion compared to lower reaction time and higher process time which tends to allow appropriate time to the activity of the catalyst.
- (ii) Navas et al. [34] confirmed that smaller diameter tube can form at longer process time. Basically, CNTs with a smaller diameter are observed at intermediate temperature and precursor pressure, which also corresponds to the conditions leading to the highest proportions of small diameters. The small diameter CNTs generally form later than the larger ones, but their onset can be accelerated by increasing the temperature or the precursor gas pressure.

Though the sample that was grown at 35 min composed of both larger (more than 25 nm) and smaller diameter MWCNTs, the smaller diameter MWCNTs are predominantly higher and it is clearly evident from Fig. 6f.

Optimization of process parameters to attain controlled diameter distribution and defectless structure

The main aim of this investigation is to study the effect of CVD process parameters on the diameter of MWCNTs and to optimize appropriate processing conditions that result defectless structure with the smallest diameter.

To attain these conditions, HRTEM, Raman spectroscopy, and thermo gravimetric analysis/differential thermogravimetry were utilized to examine the MWCNTs. From the FESEM analysis, it is found that the MWCNTs synthesized at 15-mins and 35-mins process time (Fig. 6) yielded controlled diameter distribution and defectless side wall of MWCNTs.

HRTEM analysis

Figure 8 presents HRTEM images of the MWCNTs grown at 35 min and 15 min processing time, respectively. Compared to 15 min process time, the growth of MWCNTs at 35 min process time shows defect-free, well-aligned structure and controlled diameter distribution. The little scatter in the

diameter distributions observed (Fig. 6) in both the process conditions is due to starting catalyst particles which were agglomerated in nature even before the start of the experiment. The MWCNTs tip growth mode was clearly evident in Fig. 8c indicated by an arrow mark. The MWCNTs starts reacting with the electron source that is indicated by the circle. The reaction of MWCNTs with source electrons while conducting HRTEM analysis shows the stability of the carbon that presents in Fig. 8c.

At higher temperature, acetylene decomposition tends to reduce when it reacts with the catalyst to form a solid carbon [30]; This also may be another reason for attaining controlled diameter distribution at longer process time.

Raman spectroscopy analysis

Figure 9 shows the Raman spectrum of MWCNTs grown at 35 and 15 min process time. The peaks observed at 1370, 1385 cm^{-1} correspond to the D (defective) band of MWCNTs synthesized at 15 and 35 min, respectively. The peaks at 1570, 1585 cm^{-1} are characteristics peaks due to the scattering of G band (graphitic mode) of MWCNTs synthesized at 15 and 35 min. The 680 cm^{-1} Raman shift peak was observed in MWCNTs sample synthesized at 35 min process time, which is near to the RBM mode. The presence of RBM peak is due to the shorter diameter of MWCNTs. The intensity ratio between D and G band peaks is used to evaluate the graphitization degree of CNTs. The lower value of I_D/I_G consequently relates to the high quality of MWCNTs and comparatively higher value than this corresponds to the poor structural quality, which has structural disorder [35]. The MWCNTs grown at 35 min process time show a higher degree of crystallinity compared to MWCNTs grown at 15 min process time. The observed I_D/I_G values are having good agreement with the HRTEM analysis.

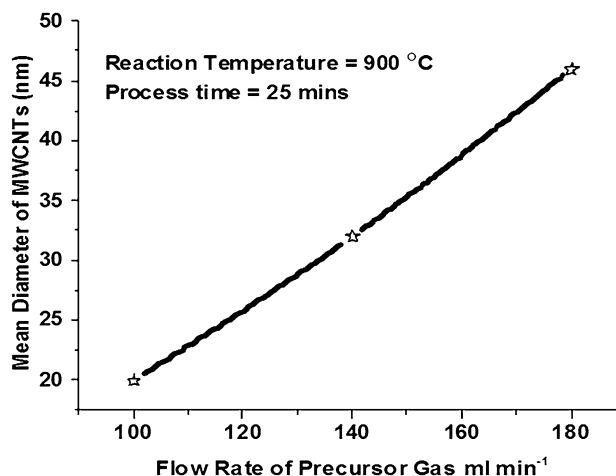


Fig. 5 Effect of precursor gas flow rate on mean diameter of MWCNTs



Thermogravimetric analysis (TGA)

Thermogravimetry was used to evaluate the thermal stability and purity of CNTs sample. Figure 10 shows the TG and DTA curve of MWCNTs grown at 15-mins and 35-mins process time. The nature of an exothermic peak is expected to occur

from the oxidation of the sample [36]. Hence, the largest exothermic peak in the DTA curve is near 680 °C (green color), which indicates the combustion of MWCNTs. The peak at 300 °C in the DTA (green color) curve is considered to be the oxidation of amorphous carbon. The TGA/DTA graph for MWCNTs grown at 15 min process time also depicted in

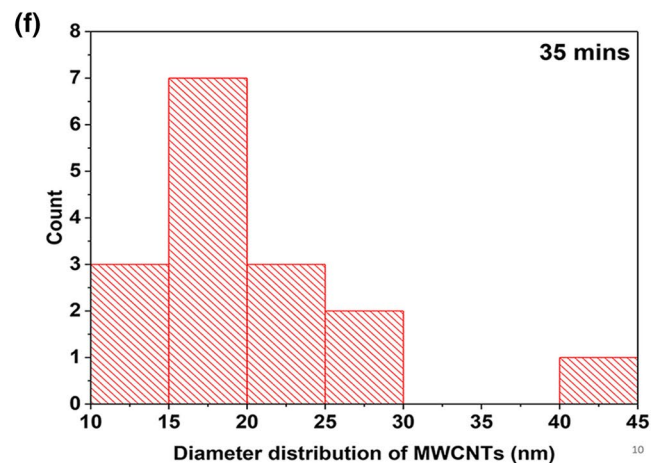
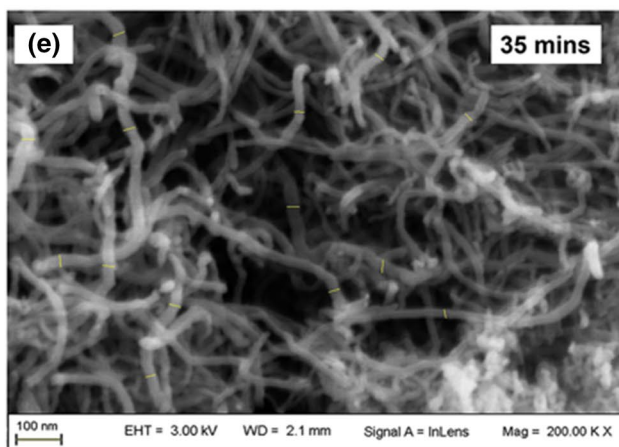
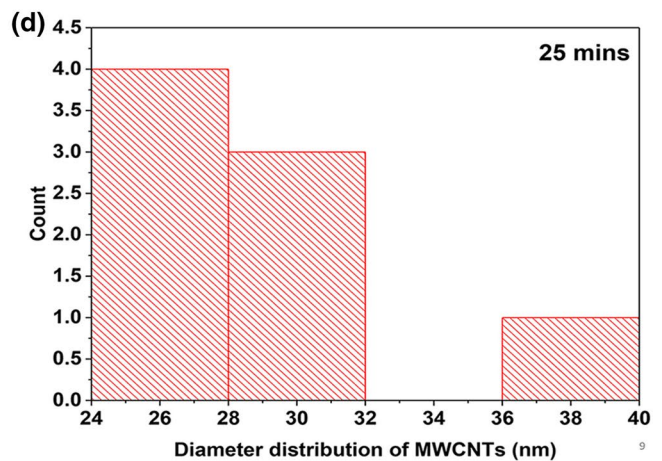
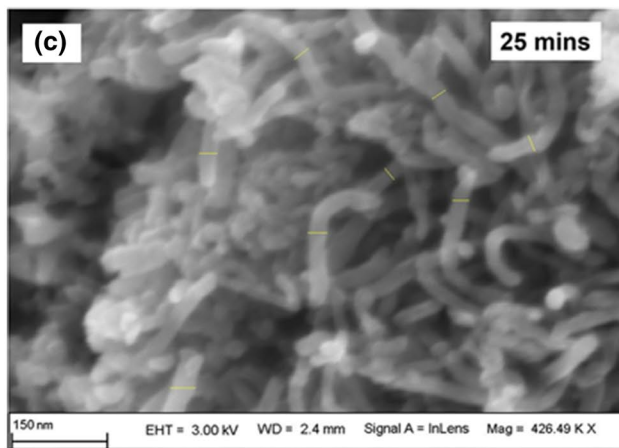
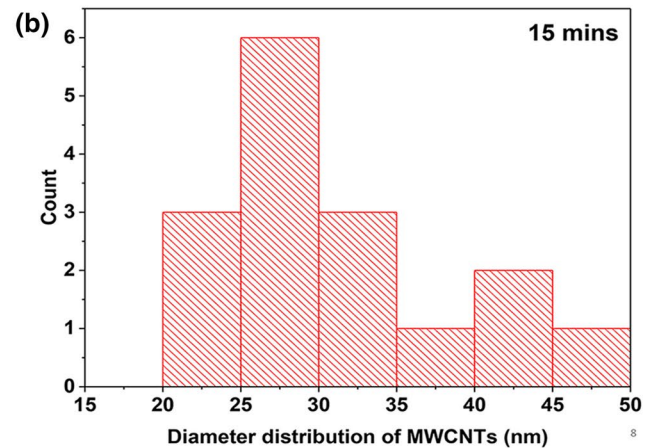
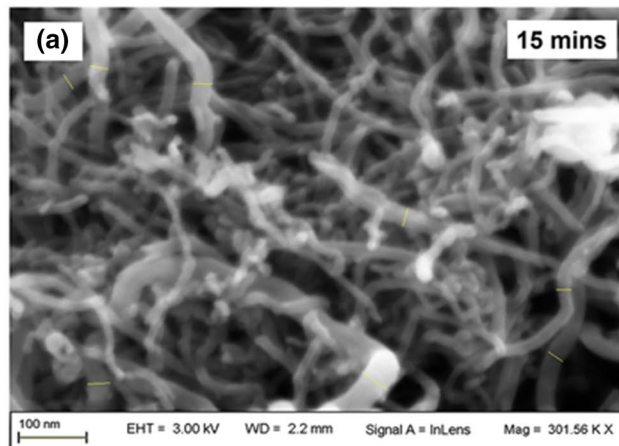


Fig. 6 FESEM image of MWCNTs grown at different processing time (a, c, e) and distribution of MWCNTs diameter as a function of processing time (b, d, f)



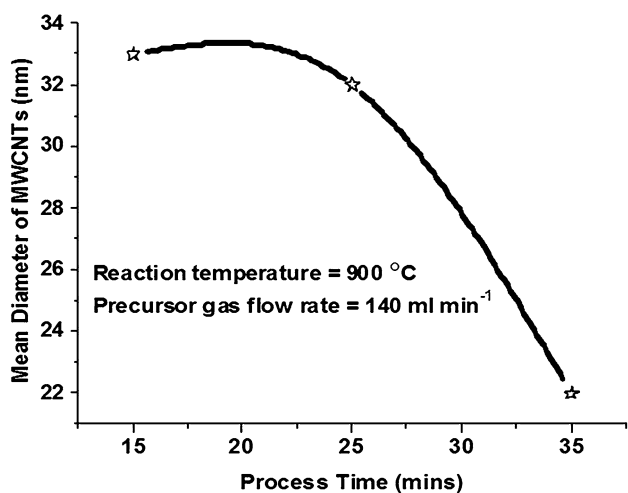


Fig. 7 Effect of processing time on mean diameter of MWCNTs

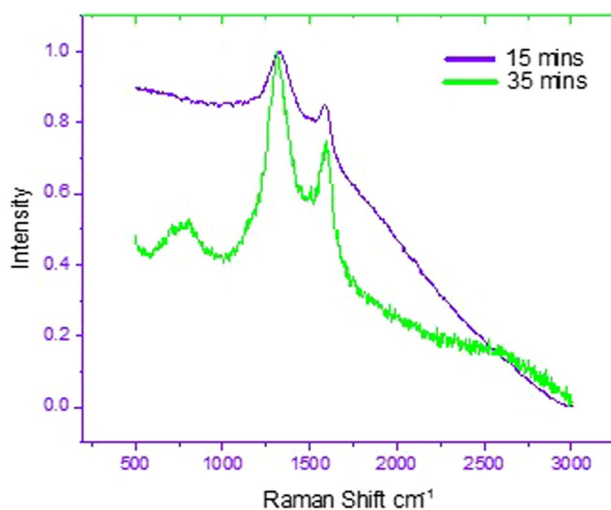


Fig. 9 Raman spectra of carbon materials synthesized at 15 and 35-mins process time

Fig. 10. The exothermic reaction peak in DTA curve (violet color) around 150 °C occurred due to the oxidation of amorphous carbon. Significant weight loss was also observed in TGA curve (violet color), which reveals the non-stability of the sample above 400 °C. The TGA analysis for MWCNTs

synthesized at 15 min and 35 min show a weight loss of 25% and 2%, respectively. From the TGA/DTA curves, it is understood that the MWCNTs grown at 35 min process time show

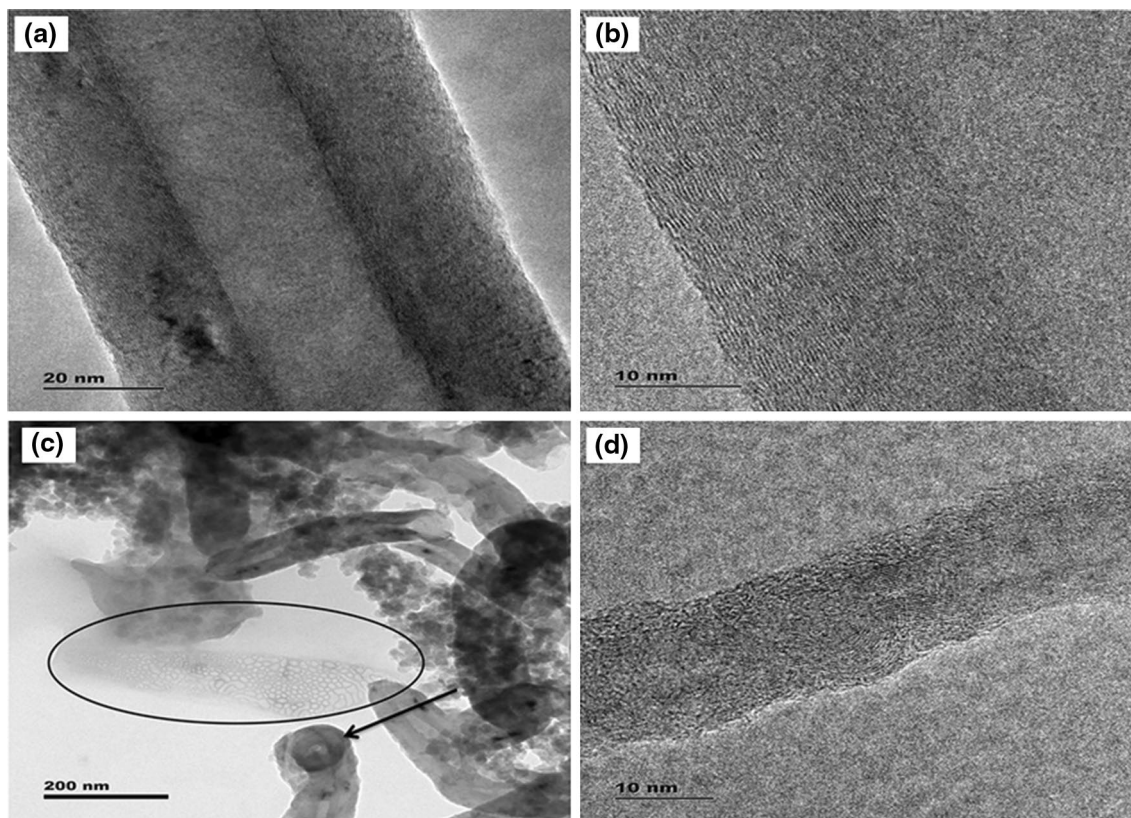
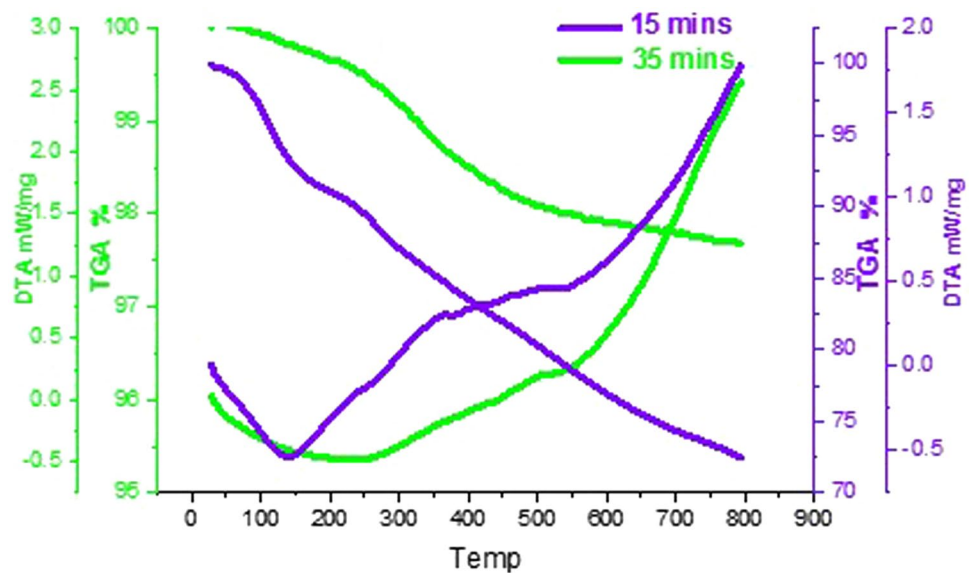


Fig. 8 HRTEM image a MWCNTs growth at 35 mins process time, b higher resolution image of a, c MWCNTs growth at 15 mins process time, d higher resolution image of c

Fig. 10 TGA/DTA profile of MWCNTs grown at 15-mins and 35-mins processing time



higher oxidative stability and form CNTs with well-aligned graphitic structure.

Conclusions

In this paper, the effect of CVD process parameters on the diameter of MWCNTs has been analyzed in detail. From this investigation, the following important conclusions are drawn.

- (i) The reaction temperature is showing directly proportional relationship with the mean diameter of MWCNTs. If the reaction temperature increases, the diameter of MWCNTs increases and vice versa. At higher reaction temperature, the catalyst particles get agglomerated and this causes an increase in diameter of MWCNTs.
- (ii) The precursor flow rate is showing directly proportional relationship with the mean diameter of MWCNTs. If the precursor flow rate increases, the diameter of MWCNTs increases and vice versa. At a higher flow rate of precursor gas (carbon gas), concentrate carbon particles increases and this lead to the faster rate of carbon diffusion and subsequently increases the diameter of MWCNTs.
- (iii) The process (reaction) time is showing an inversely proportional relationship with the mean diameter of MWCNTs. If the process time increases, the diameter of MWCNTs decreases and vice versa. At longer process time, the onset growth of smaller diameter CNTs was accelerated by the higher reaction temperature and this facilitates the growth of smaller diameter of MWCNTs.

- (iv) From the Raman peak analysis and TGA/DTA test results, it is concluded that MWCNTs synthesized at 35 min process time, has higher graphitization and higher oxidation temperature.
- (v) From this investigation, it is found that reaction temperature of 900 °C, precursor gas flow rate 140 ml min⁻¹ and process time of 35 min yielded defectless, well-aligned MWCNTs compared to all other experimental conditions.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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