

## Synthesis of carbon nanotubes by catalytic vapor decomposition (CVD) method: Optimization of various parameters for the maximum yield

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**Abstract.** This paper describes an effect of flow rate, carrier gas ( $H_2$ ,  $N_2$  and Ar) composition, and amount of benzene on the quality and the yield of carbon nanotubes (CNTs) formed by catalytical vapour decomposition (CVD) method. The flow and mass control of gases and precursor vapors respectively were found to be interdependent and therefore crucial in deciding the quality and yield of CNTs. We have achieved this by modified soap bubble flowmeter, which controlled the flow rates of two gases, simultaneously. With the help of this set-up, CNTs could be prepared in any common laboratory. Raman spectroscopy indicated the possibilities of formation of single-walled carbon nanotubes (SWNTs). From scanning electron microscopy (SEM) measurements, an average diameter of the tube/bundle was estimated to be about 70 nm. The elemental analysis using energy dispersion spectrum (EDS) suggested 96 at.wt.% carbon along with ca. 4 at.wt.% iron in the as-prepared sample. Maximum yield and best quality CNTs were obtained using  $H_2$  as the carrier gas.

**Keywords.** Carbon nanotubes (CNTs); catalytic vapor decomposition; soap bubble mass flowmeter.

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### 1. Introduction

In recent years, carbon nanotubes (CNTs) have received considerable attention due to their unique one-dimensional nanostructure and range of fascinating mechanical [1–3], physical, chemical and electronic properties [4–6]. These have a large number of potential applications which includes flat panel field emission displays [7], nanoelectronic devices [8], chemical sensors [9], hydrogen storage [10,11] and scanning probe tip [12]. High accessible surface area, low resistivity and high stability [4,13,14], makes them an excellent candidate for use as a dielectric in supercapacitors [15]. For all these investigations and applications obviously large quantity of

CNTs is needed. A cost-effective method to prepare good quality CNTs on a commercial scale, however is yet to be formulated. It motivated many research groups to investigate a number of methods including laser ablation [16], arc discharge [17] and chemical vapor decomposition [18]. Among them, the pulsed laser vaporization of a hot carbon target containing a Ni/Co catalyst and electric-arc technique using a Ni/Y catalyst have been known to give good quality and high yield CNTs. However, these methods are not economically viable as these require a huge capital investment and thus, difficult to commercialize for large-scale synthesis.

To date, catalytic vapor decomposition (CVD) of hydrocarbons catalysed by metallocenes only has a potential to scale up to the commercial level preparation [19,20]. One of the crucial parameters which decides the quality and yield have been however, the rate of mass transfer of precursor vapors [19,21,22]. It is decided by the flow and compositions of the carrier gases carrying precursor vapors. Commercial mass-flow controllers are available in the market. These are however very expensive. For that purpose, we modified a classical soap bubble flowmeter, which not only successfully controlled the flow of individual gases but also their mixtures. It can be made locally and with the help of this, CNTs can be prepared on a large scale in a common laboratory. We optimized the various parameters to get almost 96% yield of uniformly dispersed, 70 nm diameter CNTs.

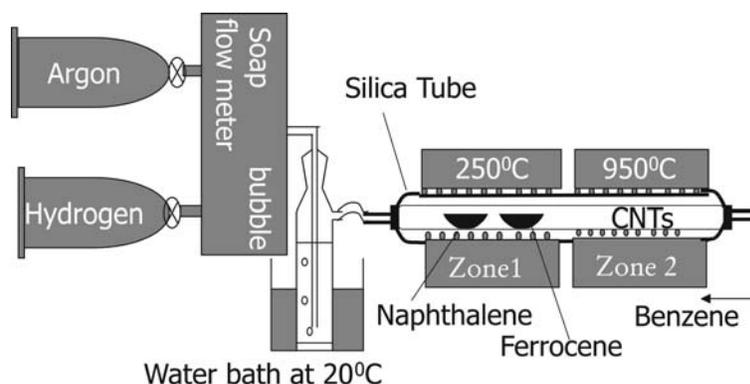
## **2. Experimental**

### *2.1 Materials*

Ferrocene (fluka), naphthalene (LR S.D. fine), benzene (for synthesis, Merck), xylene (AR grade, S.D. fine) and all the other chemicals were of analytical reagent grade and used as received without any further purification. Ar and H<sub>2</sub> gases were procured from India Oxygen Limited and of highest possible purity (O<sub>2</sub> < 2 ppm).

### *2.2 Set-up for catalytic vapor decomposition (CVD)*

Set-up used for the synthesis of CNTs is schematically represented in figure 1. Similar type of set-up has been reported by many groups [19,23,24]. It typically consists of a two-zone furnace (canthal elements, Therlack, India) with alumina tube running between the two zones. A 1.4 m long fused silica tube (outer diameter 2.5 cm and wall thickness 2 mm) having standard B34 joints on both the ends was placed into the furnace as shown in figure 1. In zone I (zone near the input) 100 mg naphthalene and 100 mg ferrocene in separate fused silica boats were introduced as shown in figure 1. After flushing the tube with dry Ar gas (1.0 ml s<sup>-1</sup>) for an hour, the temperature of zone II was elevated to 950°C. This temperature was chosen on the basis of earlier reports [25–27] and our own results (not shown) about the yield of CNTs as a function of temperature in the range 650 to 1000°C, which was maximum at 950°C. Ferrocene and naphthalene were vaporized by raising the temperature of zone I to 250°C, which is well above the sublimation temperature of ferrocene (174°C) and naphthalene (82°C). The desired gas or the mixture of gases



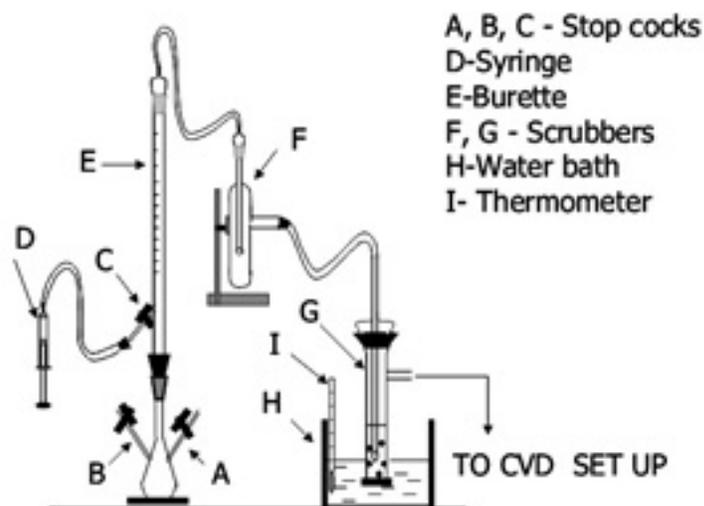
**Figure 1.** CVD set-up for the synthesis of CNTs.

of known flow rates along with benzene vapors were introduced into the furnace, which also carried away the ferrocene and naphthalene vapors from zone I to zone II. To facilitate the flow control and composition of gases, modified classical soap bubble meter was used as shown in figure 2. It is a common soap bubble flowmeter but having a provision to introduce two gases either individually or simultaneously. On calibration, the total flow rate was confirmed to be a linear combination of two flow rates. The input pressure of both the gases was kept at 10 psi ( $0.73 \text{ kg cm}^{-2}$ ). For few experiments, the vapor load was changed at a constant flow rate. It was achieved by raising or lowering the temperature of the scrubber containing benzene ('G' in figure 2). The amount of benzene consumed was estimated by measuring the change in liquid level in the scrubber. After the stipulated time, the furnace was switched off and allowed to cool down to room temperature in the presence of the gas flow. The black colored product deposited on the inner wall of the tube was scratched off and stored in a vacuum desiccator for further analysis.

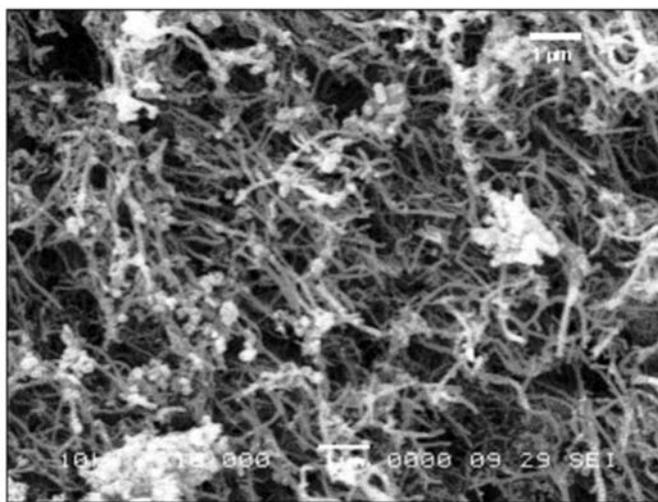
Raman spectrum of CNTs was recorded using the 532 nm line from a diode-pumped  $\text{Nd}^{3+}$ : YAG laser (SUWTECH laser, Model G-SLM-020 from Shanghai Uniwave Technology Co. Ltd). The spectrometer consisted of a single monochromator of focal length 0.9 m. The detector was CCD ( $1024 \times 256$  pixels) from Andor Technology. All the measurements were carried out with the exposure time of 50 s. Effect of various parameters on the morphology of CNTs was studied by recording SEM images of samples deposited on fused silica plate using JEOL JSM-6360 SEM instrument. To obtain adequate conductivity, platinum was sputtered on the sample.

### 3. Results and discussion

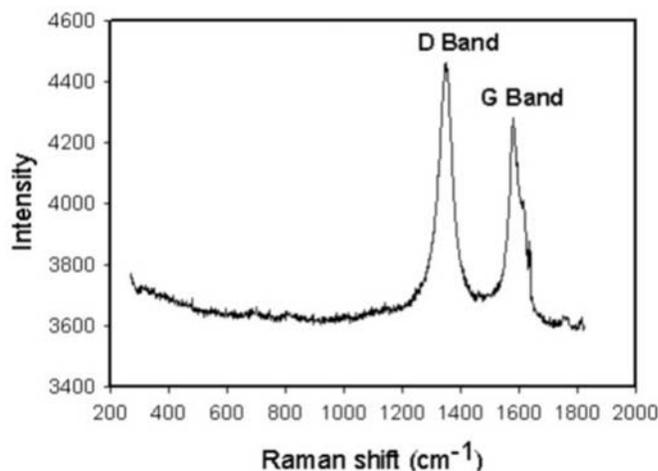
Besides formation of CNTs, chemical vapor decomposition (CVD) of hydrocarbons on metal catalysts is known to form an undesirable filamental and amorphous carbon [28]. Aromatic hydrocarbons are however known to play a different kind of chemistry. Endo *et al* were among the first to report the formation of CNTs by



**Figure 2.** Schematic of modified soap bubble flow meter. Two gases were introduced simultaneously through stop-cocks, A and B. The soap solution was injected at point C using syringe D. The rate of gas flow was measured based on a travel time of the trapped bubble in the burette E. Unused soap solution was eventually collected in the bottom of the flask. Trap F avoids the soap solution to enter in the system. The gases were then passed through the scrubber G containing benzene. The temperature of this scrubber was maintained using water bath H.



**Figure 3.** SEM image of the product deposited on fused silica plate in the presence of Ar flow rate ( $1.0 \text{ ml s}^{-1}$ ). The tubular structures suggested the formation of CNTs.

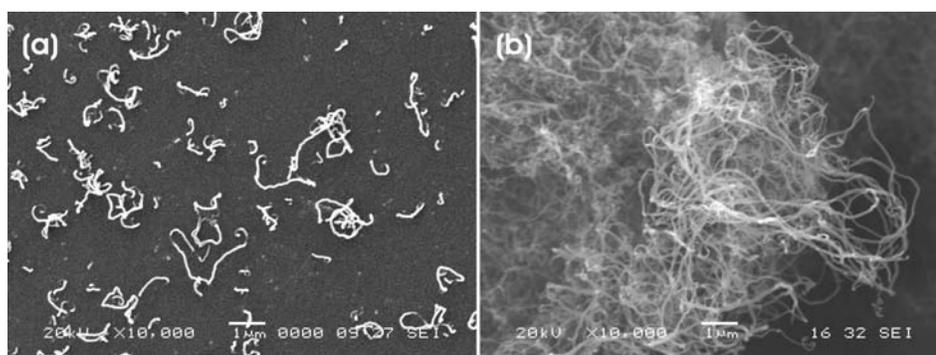


**Figure 4.** Raman spectrum recorded on as-prepared sample produced in Ar atmosphere at a flow rate of  $1.0 \text{ ml s}^{-1}$ .

CVD, using benzene as a precursor [23]. Metallocenes and in particular ferrocene have been used to increase the yield of CNTs [29–31]. Ferrocene is known to decompose into iron nanoparticles, which act as a seed to initiate the formation of tubular structure. We have used the mixture of benzene and naphthalene vapors as precursors, as the yield was better compared to the one obtained with individual precursors. Keeping these parameters constant, the effect of carrier gases and their flow rates on CNT formation was investigated.

SEM recorded on the product formed in the presence of a pure Ar gas ( $1.0 \text{ ml s}^{-1}$ ) is shown in figure 3. As seen, the substrate is occupied with densely packed, tubular structure having average tube-diameter of about 70 nm. Not much variation in size or packing density was observed in the micrographs recorded at various other areas. Small amount of amorphous carbon in the form of globules is also seen in the picture. The bright, spherical structures at one of the ends of most of the tubes are attributed to the iron nanoparticles formed on decomposition of ferrocene. It was further supported by elemental analysis using EDS measurement, where the presence of an average 96 at.wt.% carbon and 4 at.wt.% iron were observed.

To confirm the tubular structure seen in SEM were nothing but the CNTs, Raman spectra were recorded on these samples. One of the typical spectra is depicted in figure 4. It shows two significant bands having peaks at about  $1582 \text{ cm}^{-1}$  and  $1354 \text{ cm}^{-1}$ . The peak at  $1582 \text{ cm}^{-1}$  referred to as ‘G’ band, is a tangential vibrational mode of graphene sheet, which is related to the E<sub>2g</sub> symmetry of graphite [32–35]. A distinct band at  $1354 \text{ cm}^{-1}$  (D band) is related to the amorphous carbon or defects in the graphene sheet. In the SEM picture, the amorphous carbon is seen to be present in a negligible amount (figure 3). Therefore, the D-band could be grossly attributed to the defects present in the graphene sheets. Thus from the Raman spectrum, the formation of multi-walled carbon nanotubes is confirmed. There was no significant difference observed among the Raman spectra recorded for other samples.



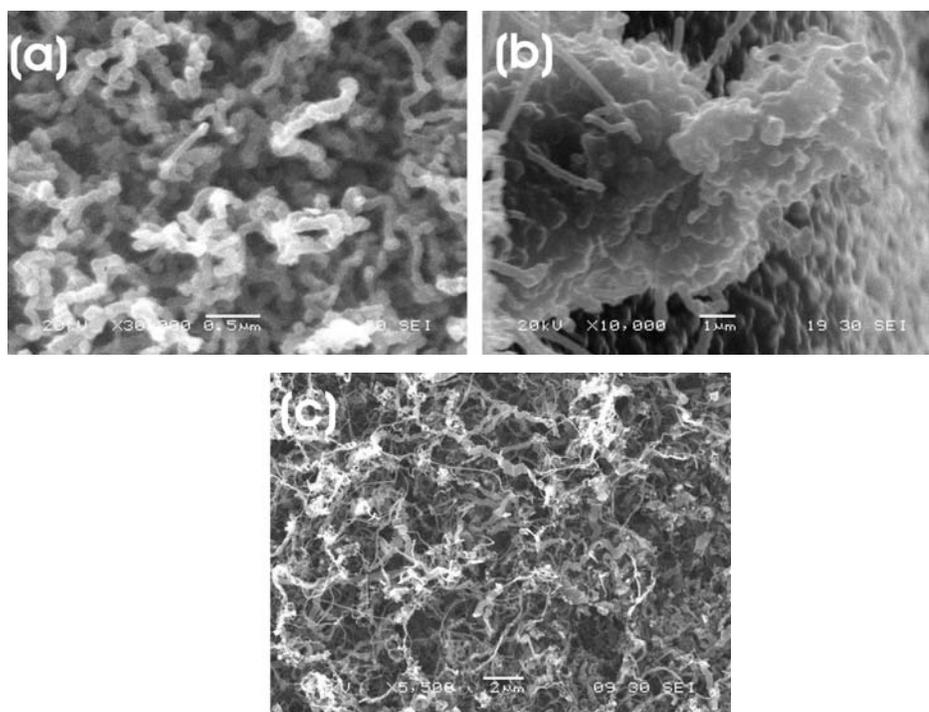
**Figure 5.** SEM images of CNTs. (a)  $N_2$  as carrier gas and (b)  $H_2$  as carrier gas.

To understand the effect of a carrier gas on the quality of a product, CVD has been carried out in the presence of nitrogen and hydrogen flow, keeping all the other experimental conditions unaltered. SEMs recorded on the products are shown in figure 5. Formation of CNTs was observed in both the cases. In the  $N_2$  flow, CNTs formed were having well-separated strands but these were very few in number. The formation of amorphous carbon was not seen in this case (figure 5a). Figure 5b depicts the SEM image recorded for the sample synthesized in  $H_2$  gas flow. In comparison to  $N_2$  (figure 5a) and Ar (figure 3), the CNTs were uniformly distributed, and have long well-separated strands. Amorphous carbon was also not apparent in the micrograph. Thus, based on these sets of experiments,  $H_2$  seemed to be a better choice among the three carrier gases used in the preparation of CNTs by CVD routes. A reason for change in morphology of CNTs as a function of the nature of carrier gas is not yet clear to us. On *prima facie*, it could be attributed to the different adsorption properties of various gases specifically at different lattice sites, which promotes or inhibits the crystal growth in a particular direction.

Though individually these carrier gases in principle led to the formation of CNTs, use of mixture of Ar and  $H_2$  gave unexpected results. The proportions used and other experimental details are listed in table 1. The corresponding SEM recorded on the product is shown in figure 6. Different morphology of CNTs was observed on changing the proportion of gases in their mixture. In the presence of 10%  $H_2$  and 90% Ar, these were having helical or twisted structure further entangled in the form

**Table 1.** Proportion of  $H_2$ :Ar used for the preparation of CNTs in gas mixture. The temperature of scrubber was  $20^\circ C$ .

Flow rate of $H_2$ ( $ml\ s^{-1}$ )	Flow rate of Ar ( $ml\ s^{-1}$ )	Collective flow rate of Ar and $H_2$ ( $ml\ s^{-1}$ )	$H_2$ : Ar
0.420	0.445	0.80	50 : 50
0.084	0.832	0.87	10 : 90
0.788	0.091	0.88	90 : 10

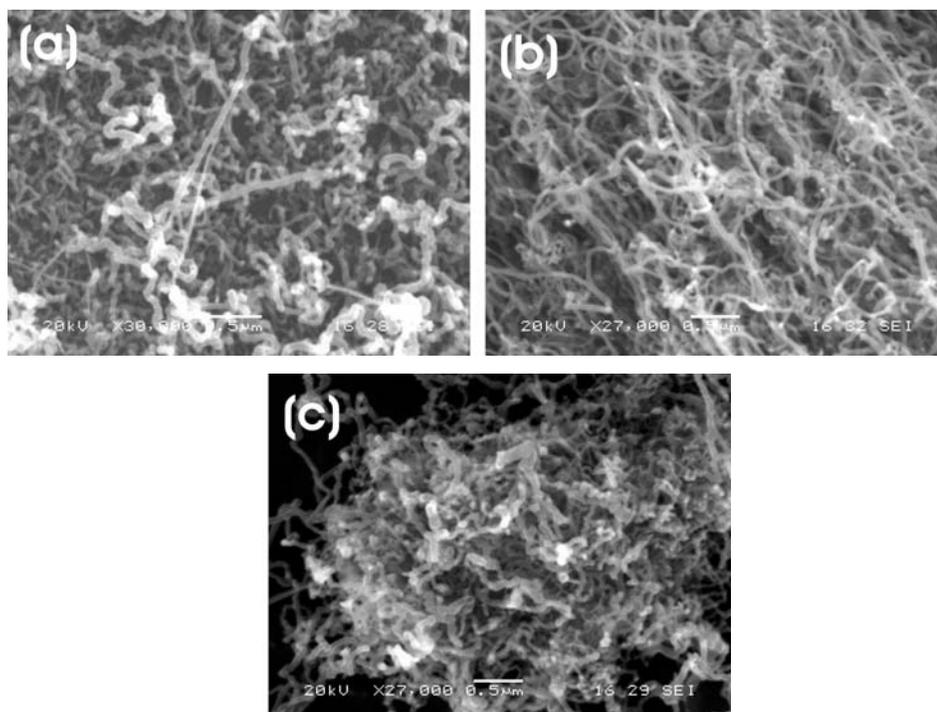


**Figure 6.** SEM images of CNTs. (a) 10% hydrogen and 90% argon, (b) 50% hydrogen and 50% argon and (c) 90% hydrogen and 10% argon.

of solid mass as seen in figure 6b. On changing the proportion to 50% hydrogen and 50% argon, these were observed to be in helical shape and still entangled as seen in figure 6a. Nevertheless, the morphology is much more open compared to 10% H<sub>2</sub> and 90% Ar. Increasing the proportion of H<sub>2</sub> to 90% led to the formation of more straight CNTs. These changes in the morphology have been attributed to the change in morphology of iron nanoparticle seeds which is a function of reducing atmosphere.

Effect of flow rate on morphology and yield have also been studied. The results are depicted in figure 7. As can be seen, the higher flow rate of carrier gas led to the formation of amorphous carbon in a higher proportion. Typically, flow rate of 1.96 ml s<sup>-1</sup> gave an optimum yield and less quantity of amorphous carbon. In the case of higher flow rate perhaps sufficient number of nuclei were not available for the reaction which might led to the formation of amorphous carbon in higher proportions.

A vapor load of benzene was found to be an important factor in deciding the morphology and the yield of CNTs. It is directly proportional to the vapor pressure of benzene. In our case, it was controlled by the temperature of scrubber, at a given flow rate of carrier gas. The experiments were carried out at three different temperature conditions, namely, 15, 20 and 35°C. The corresponding consumption rates were 1.5, 3.3 and 4.6 ml h<sup>-1</sup>, respectively. Figure 8 shows the SEM pictures



**Figure 7.** SEM images of CNTs prepared as a function of hydrogen flow rate. (a)  $0.9 \text{ ml s}^{-1}$ , (b)  $1.96 \text{ ml s}^{-1}$ , (c)  $4.065 \text{ ml s}^{-1}$ .

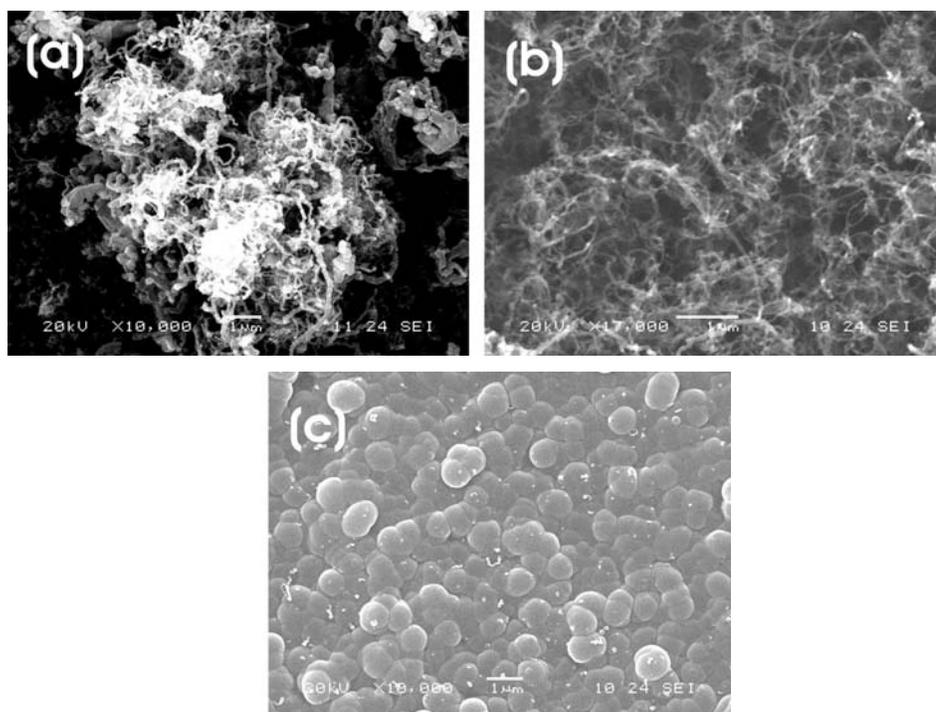
recorded on the products obtained with these three flow rates. From consumption rates  $1.5 \text{ ml h}^{-1}$  (figure 8a) to  $3.3 \text{ ml h}^{-1}$  (figure 8b), there is not much change in morphology of the CNTs. However, in the case of  $4.6 \text{ ml h}^{-1}$  the formation of globular structures perhaps amorphous carbon was observed. This is attributed to the availability of insufficient catalyst at steady state.

#### 4. Conclusion

There are lots of reports on synthesis of CNTs by CVD method. Many factors have been taken into consideration to synthesize good quality as well as quantity of CNTs. In our case, the desired quality CNTs were resulted from 100% hydrogen at a flow rate of  $1.96 \text{ ml s}^{-1}$  and vapor load of  $3.3 \text{ ml h}^{-1}$ . These parameters were controlled by simple set-ups which can be fabricated in any common laboratory.

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**Figure 8.** SEM images of CNTs showing the effect of consumption rate of benzene on the yield at  $1.96 \text{ ml s}^{-1}$  flow rate of hydrogen.

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