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Large scale synthesis of bundles of aligned carbon nanotubes using a natural precursor: turpentine oil

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Bundles of aligned carbon nanotubes (ACNTs) have been synthesised by spray pyrolysis of turpentine oil (inexpensive precursor) and ferrocene mixture at 800°C. Turpentine oil ($C_{10}H_{16}$), a plant-based precursor was used as a source of carbon and argon as a carrier gas. The bundles of ACNTs have been grown directly inside the quartz tube. The as-grown ACNTs have been characterised through X-ray diffraction, Raman spectroscopy, scanning and transmission electron microscopic techniques. Scanning electron microscope images reveal that the bundles of ACNTs are densely packed and are of ~70–130 μm in length. High-resolution transmission electron microscopy and Raman spectroscopy observations indicate that as-grown multi-walled carbon nanotubes (CNTs) are well graphitised. These CNTs have been found to have outer diameters between ~15 and 40 nm. This technique suggests a low-cost route for the large-scale formation of ACNTs bundles.

Keywords: aligned carbon nanotubes bundles; spray pyrolysis; chemical vapour deposition

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable interest since their first synthesis in the early 1990s [1]. Due to their one-dimensional structure, CNTs exhibit various outstanding properties, for example, electrical and mechanical properties that are quite attractive to nanotechnology [2,3]. Aligned carbon nanotubes (ACNTs) represent an important architecture of CNTs because they can be used directly as field emitters in flat panel displays as reinforcing agents in composite materials, etc. [4,5]. It has also been proposed to use ACNTs as highly efficient media for high harmonic generation [6]. For such an application, large arrays of ACNTs are necessary. The most well known methods for synthesising CNTs are arc discharge, laser ablation and chemical vapour deposition (CVD) [7–10]. Progress in growing ACNTs have been made with a combined approach of precatalyst patterning and CVD [10–17]. The CVD method (in which hydrocarbon is pyrolysed in the presence of transition metal catalysts) has attracted attention due to the possibility of producing nanotubes on a commercial scale. The key

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parameters involved in growing CNTs using CVD are the types of hydrocarbons and catalysts used and the temperature at which the reaction takes place. The production of aligned multi-walled CNTs (MWNTs) was first reported by Li et al. [11] using mesoporous silica containing iron nanoparticles. Ren et al. [12] reported the production of well-aligned CNTs from plasma-enhanced CVD of ethylene on Ni-coated glass substrate, while Sen et al. [14] produced bundles of ACNTs using metallocene sources.

To date, several carbon precursors such as methane, acetylene, benzene, xylene, toluene, etc. have been used as a carbon feedstock to synthesise CNTs [10–16]. These carbon precursors are related to fossil fuels and there may be a crisis for these precursors in the near future. There are few reports on the synthesis of CNTs from natural precursors, e.g. turpentine oil ($C_{10}H_{16}$), camphor ($C_{10}H_{16}O$) and eucalyptus oil ($C_{10}H_{18}O$) [18–25]. The advantages of using natural precursors as a carbon feedstock for synthesising CNTs is that they are inexpensive and have no chance of shortage in the near future. Using these natural precursors as a carbon feedstock, Ghosh et al. [21], Kumar and Ando [22,23] and Afre et al. [19,20] prepared CNTs by thermal decomposition of camphor and turpentine oil. The CNTs were synthesised by catalytic decomposition of turpentine oil over finely dispersed Fe, Co catalysts at 700°C under nitrogen atmosphere [20]. In the CVD method, the nanotubes are grown on quartz in the form of either a specific substrate or the reactor/tube wall. Recently, Afre et al. [19] have used spray pyrolysis method and prepared ACNTs from ferrocene and turpentine oil mixture on quartz and silicon substrates. The ferrocene acts as an *in situ* Fe catalyst precursor and forms nanosized Fe particles for the growth of ACNTs on silicon and quartz substrates. Despite the aforementioned efforts aiming at efficient synthesis of CNTs, further research is necessary to improve yield and purity of CNTs. The aim of this investigation is to grow bundles of ACNTs on a large scale and with high purity by spray pyrolysis of a ferrocene and turpentine oil mixture directly onto the quartz tube.

2. Experimental

The synthesis of ACNTs was carried out using the spray pyrolysis-assisted CVD method. In the spray pyrolysis method, pyrolysis of the carbon precursor with a catalyst and deposition occur in one step. Turpentine oil (derived from the resin of pine trees) has a purity of ~99.5% (Sigma Aldrich) and was used as carbon source. Ferrocene [$Fe(C_5H_5)_2$] (Alfa Aesar, high purity ~100%) was used as a source of Fe which acts as a catalyst for the growth of CNTs. The spray pyrolysis setup consisted of a nozzle (inner diameter ~0.5 mm) attached to a ferrocene–turpentine supply used for releasing the solution into a quartz tube (700 mm long with an inner diameter of 25 mm), which was mounted inside a reaction furnace (300 mm long) [26]. The outer part of the quartz tube was attached with a water bubbler. In a typical experiment, the quartz tube was first flushed with argon (Ar) gas in order to eliminate air from the quartz tube and then heated to a reaction temperature. The precursor solution (ferrocene and turpentine oil) was sprayed into the quartz tube, using Ar gas. The concentration of ferrocene in turpentine oil was ~25 mg/ml. The solution was sonicated for 5 min to prepare the homogeneous mixture. The flow rate of Ar was ~100 sccm. The experiments were conducted at different temperatures (~700–900°C) at atmospheric pressure, with a typical reaction time of 15 min for each deposition. After deposition, the furnace was switched off and allowed to cool down to room temperature

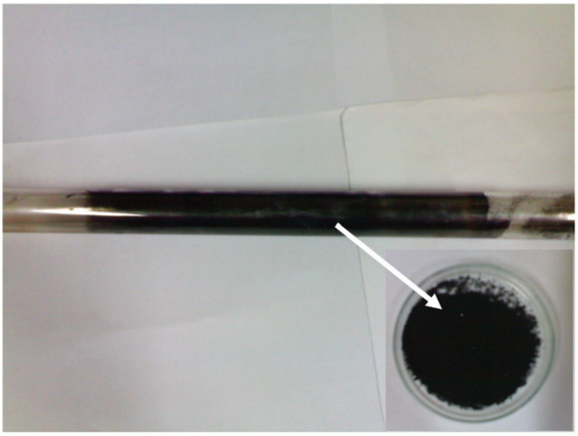

Figure 1. Photograph showing the deposition of CNTs inside the quartz tube. Inset image shows the CNTs soot.

under Ar gas flow. A uniform black deposition on the inner wall of the quartz tube at the reaction hot zone was observed (Figure 1). The black deposition in the form of carbon soot (inset of Figure 1) was removed from the quartz tube.

The as-grown carbon materials were characterised by using X-ray diffractometer (XRD) (Philips PW 1710), scanning electron microscope (SEM) (Philips XL 20) and transmission electron microscope (TEM) (Tecnai G_2 20) equipped with an X-ray energy dispersive spectrometer. For SEM observation, the black soot like material was directly mounted to the sample holder with silver glue, which is electrically conductive. Samples for TEM studies were prepared by dispersing a small amount of black soot-like materials in ethanol using a sonication bath for 10 min. This suspension was dropped onto a holey carbon grid and dried. A Raman spectrum of the as-grown sample was measured by Raman spectrometry (Renishaw, model no. H 45517) using an argon ion laser ($\lambda = 514$ nm).

3. Results and discussion

Spray pyrolysis of the ferrocene and turpentine oil solution at ~800°C leads to a large amount of carbon soot-like deposition along the total heating zone (~15 cm) inside the quartz tube (Figure 1). Microstructural investigations of as-grown samples were carried out using SEM and TEM techniques. The SEM study (Figure 2) reveals that the CNTs exist in the form of bundles made up of ACNTs. As can be seen, the as-grown ACNTs bundles are clean and free from other carbonaceous materials. The length of the CNTs bundles varies from ~70 to 130 μm (Figure 2(a)). The magnified view of CNTs bundles is shown in Figure 2(b). This micrograph reveals a dense, self-aligned growth of CNTs bundles. Such growth has been found for all bundles of CNTs. The dense ordered packing in the form of aligned CNTs arises due to van der Waals interaction between the CNTs. The growth temperature varied between 700 and 900°C. Figure 3 illustrates the SEM images of the CNTs samples grown at different temperatures. There is no growth

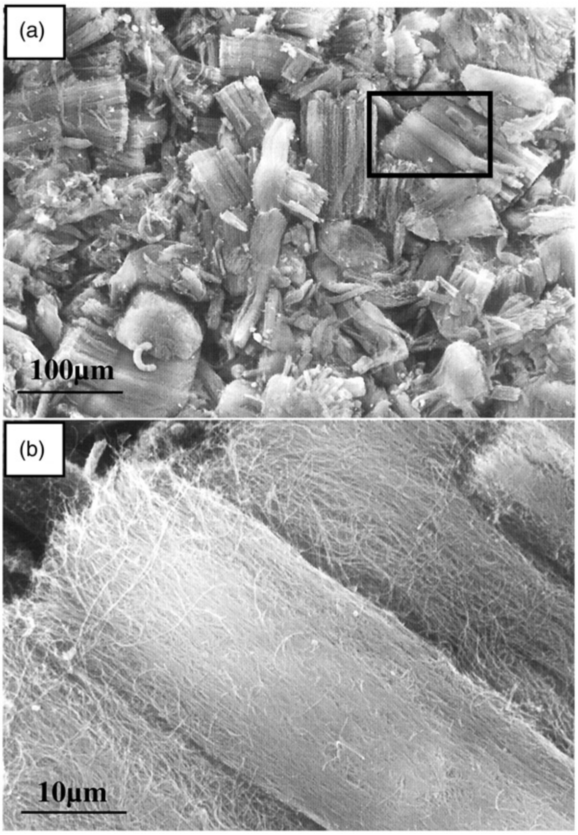

Figure 2. SEM images of as-grown CNTs at 800°C: (a) bundles of ACNTs and (b) the magnified SEM image of the rectangular marked region in (a).

of CNTs at 700°C because this temperature is not sufficient to pyrolyse the carbon source. On the other hand, at 750°C, few CNTs bundles were found to grow (Figure 3(a)). The formation of CNTs bundles is low because at this temperature the carbon source decomposes partially leading to the formation of carbonaceous materials (e.g. amorphous carbon). At 900°C, the quantity of CNTs bundles within the sample has decreased (Figure 3(b)) and thick nanotubes have been formed (inset of Figure 3(b)). The diameter of nanotubes increased with increasing temperature suggesting an increased mobility of the Fe particles on the quartz tube, leading to larger Fe clusters. We repeated the experiment at ~800°C temperature several times to ensure the reproducibility of the formation of ACNTs bundles.

Figure 4(a) and (b) shows the TEM images of CNTs grown at ~800°C. It can be noticed that amorphous carbon and metal particles are nearly absent. The TEM images show the high-density growth of CNTs. From TEM micrograph (Figure 4(a)), CNT density was estimated to be of the order of $\sim 10^{10}$ nanotubes/cm^2. The nanotubes are found to be multi-walled. These CNTs have an empty and uniform central core. A significant observation is that by using spray pyrolysis in this work, unlike in an earlier report [16,18]

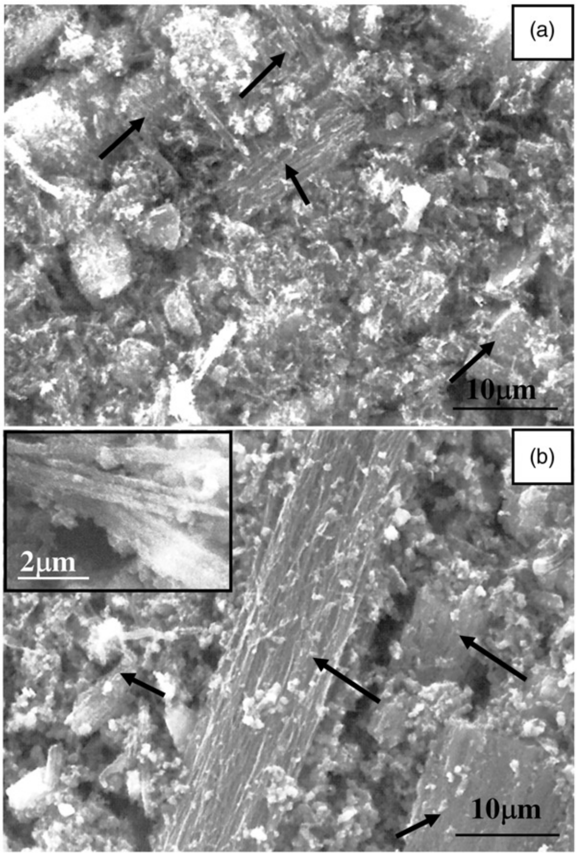

Figure 3. SEM images of CNTs bundles grown at (a) 750°C and (b) 900°C. Inset SEM image shows the presence of thick CNTs. Some of the CNTs bundles are marked by arrows.

on the formation of CNTs, instances of Fe filling in CNTs were found to be nearly absent (Figure 4(b)). The selected area electron diffraction (SAED) pattern taken from the CNTs shows the presence of sharp graphitic (00.2) and (00.4) reflections (Figure 4(c)). Figure 5 shows the diameter distribution of as-grown CNTs obtained from a TEM image (Figure 4(b)). The outer diameter of the CNTs is about 15–40 nm. The high-resolution TEM (HRTEM) images of as-grown CNTs are shown in Figure 6(a) and (b). HRTEM image (Figure 6(b)) reveals well-graphitised MWNT layers at $d_{00.2}$ with lattice spacing of ~0.34 nm. The nanotube exhibits ~70 concentric graphene cylinders for which the straight fringes indicate a high degree of crystallinity. Energy dispersive X-ray (EDX) analysis of as-grown CNTs at 800°C revealed the iron content to be ~0.11 wt%. This is in agreement with our TEM observation that the metal particle in our sample, is negligible. Thus, in this method, we do not need further purification treatments.

It is known that for the preparation of CNTs via the CVD method, the growth of nanotubes depends upon the catalyst used in the process, of which the morphology and composition would determine the microstructure, diameter and morphology of

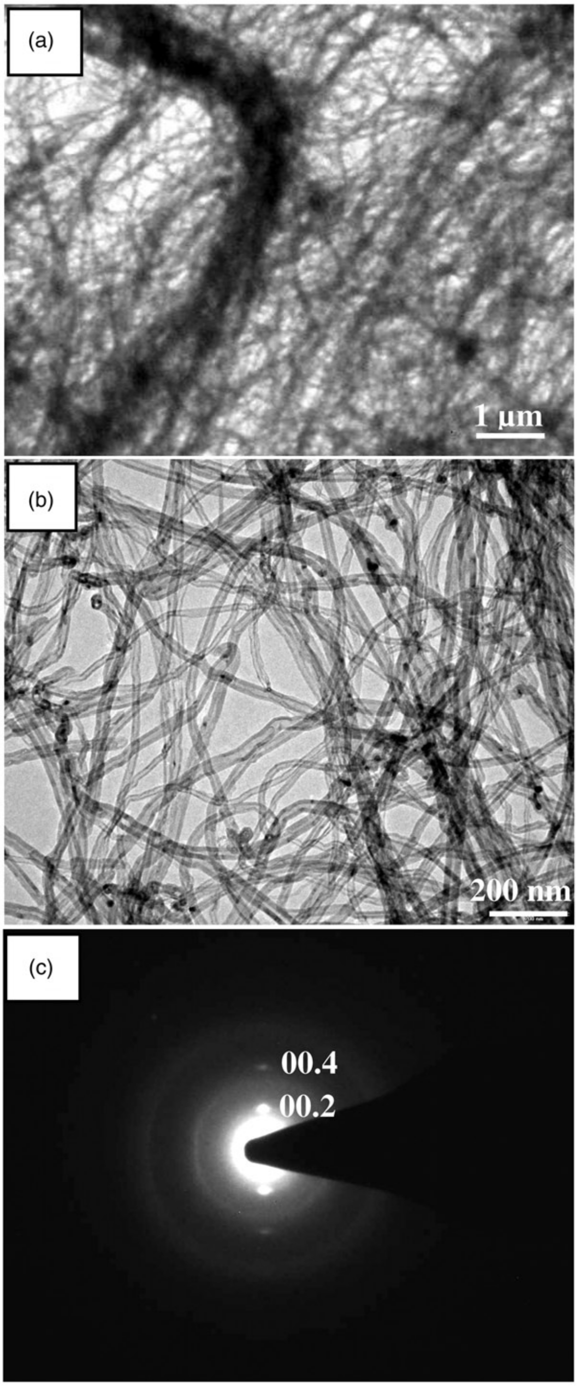

Figure 4. TEM images of as-grown CNTs at ~800°C, showing the high yield and clean CNTs (a), (b). Selected area electron diffraction pattern of the as-grown CNTs (c).

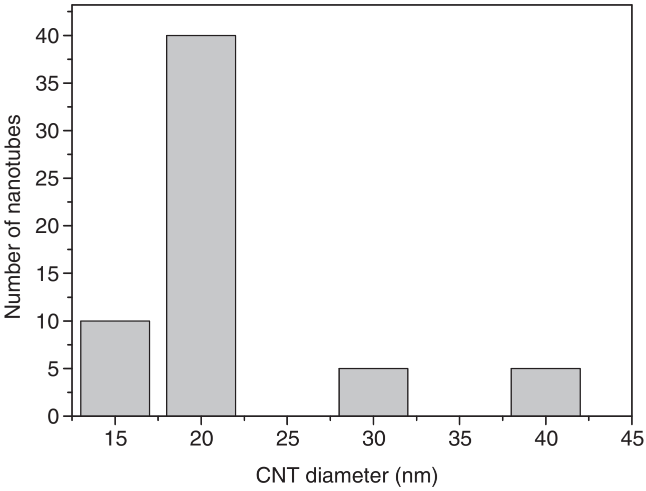

Figure 5. The diameter distribution of CNTs grown at 800°C.

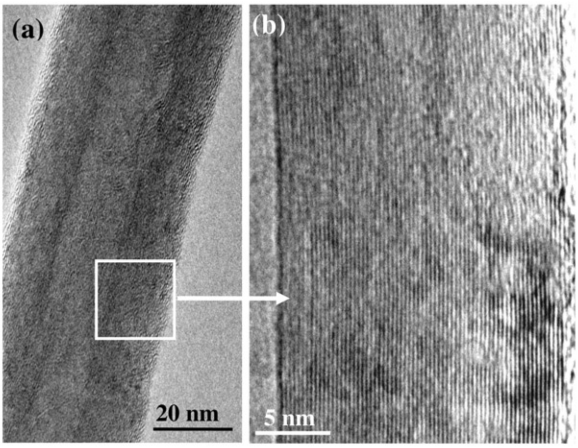

Figure 6. HRTEM image of as-grown CNT at 800°C (a). High-resolution image of a marked region showing well-graphitised nanotube layers (b).

CNT products [16,17,27]. In this study, ferrocene, a metal organic molecule was used as a catalyst. The as-grown CNT sample was characterised by XRD. Figure 7 shows the typical XRD pattern of CNTs grown at ~800°C. The peaks are indexed to be the (00.2) and (10.1) reflections of hexagonal graphite. The presence of the (00.2) peak in the XRD spectra of CNTs indicates the concentric cylindrical nature of the graphene sheet ($d_{00.2} = 0.342\,\text{nm}$) nested together and the nanotubes are multi-walled in nature. The interlayer spacing ($d_{00.2} = 0.342\,\text{nm}$) found by XRD is consistent with that obtained ($d_{00.2} \sim 0.34\,\text{nm}$) from HRTEM and is characteristic of CNTs. The purity of as-grown CNTs is better than that obtained by CVD using conventional hydrocarbon [16].

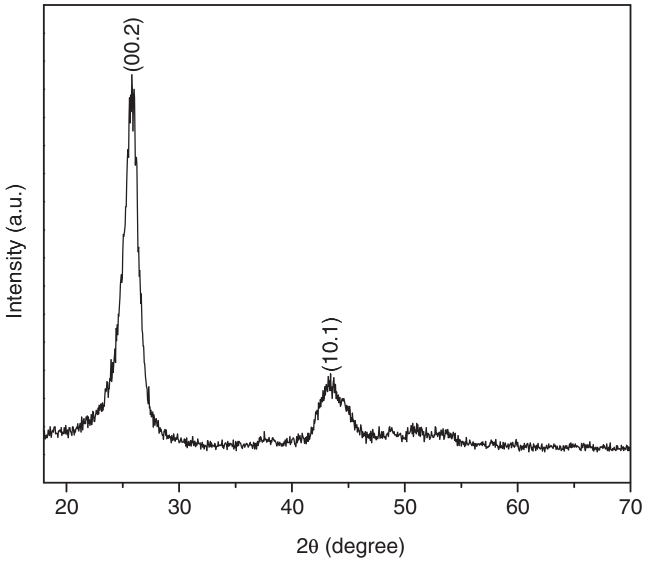

Figure 7. XRD pattern of as-grown CNTs at ~800°C.

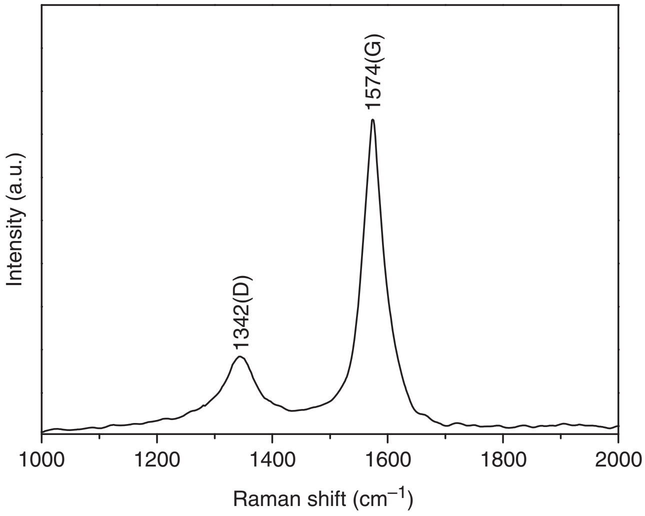

Figure 8. Raman spectra of as-grown CNTs at ~800°C.

Raman spectroscopy is an important tool for studying CNTs samples, which provides information about the structure and the presence of disorder in the sample. Raman spectra of as- grown CNTs was taken by an Ar ion laser of wavelength 514 nm. Figure 8 shows the representative Raman spectra of a CNTs sample as-grown at ~800°C. In the Raman-shift range 1000–1800 cm^{-1}, two peaks are observed at 1342 and 1574 cm^{-1} corresponding to D and G bands, respectively. The G band corresponds to the tangential stretching (E_{2g})

mode of highly oriented pyrolytic graphite and suggests the CNTs are composed of crystalline graphitic carbon. The higher intensity of the G band peak indicates the higher degree of graphitisation/crystallinity. This is in agreement with our HRTEM observations. On the other hand, the D band at 1342 cm^{-1} originates from disorder in the sp^2-hybridised carbon and indicates lattice distortions in the curved graphene sheets, tube ends, etc. The intensity ratio of D and G peaks (I_D/I_G) is used to characterise the purity of CNTs. Generally, lower I_D/I_G value indicates a higher degree of graphitisation [17,28]. The I_D/I_G value of as-grown CNTs is ~0.245. This value reveals a higher degree of graphitisation when compared to those values reported for CNTs grown by thermal decomposition of acetylene, etc. (e.g. $I_D/I_G \sim 0.85$–1.3) [29] and spray pyrolysis of natural precursors (e.g. turpentine, eucalyptus oil and camphor) ($I_D/I_G \sim 0.3$–0.67) [21,23,25].

The spray pyrolysis experiments were carried out at different temperatures and deposition times. It was observed that a temperature below 750°C and a deposition time less than 15 min is not suitable for growth of CNTs. In this experiment, the ferrocene and turpentine oil gets atomised via the spray nozzle and are sprayed through a carrier gas (Ar). As the accelerated ferrocene–turpentine droplets hit, the hot clusters (coming from decomposition of ferrocene) get deposited on the surface of the quartz tube. The carbon species (released from the decomposition of turpentine oil and also from ferrocene) are adsorbed on to the surface of Fe clusters and diffuse rapidly along the axial direction of the nanotube resulting in the formation of CNTs. Thus, the copious nucleation of Fe catalytic particles facilitates the growth of CNTs in the aligned form of the nanotubes.

The concentration of ferrocene in turpentine oil influences the purity and yield of CNTs bundles. The optimum concentration of ferrocene in turpentine oil was found to be ~25 mg/ml. The flow rate of carrier gas (Ar) is another important factor. The modification of this rate can change the catalyst-feeding rate. This in turn influences the size of metal catalyst particles. An appropriate flow rate is needed to ensure formation of fine catalyst particles leading to the formation of CNTs. The optimum flow rate of the ferrocene and turpentine oil mixture has been 0.5 ml/min. Synthesis carried out at ~800°C was found to produce bundles of aligned CNTs in a large scale. Concentration of ferrocene in turpentine oil of 25 mg/ml and a temperature of 800°C with Ar gas flow rate of ~100 sccm are the optimum conditions for producing extreme bundles of high-purity ACNTs.

4. Conclusion

The bundles of ACNTs have been successfully prepared in a large scale with low cost by the spray pyrolysis of ferrocene and turpentine oil mixture at ~800°C under an Ar atmosphere. Dense ACNT bundles have been prepared inside the quartz tube. The as-grown multi-wall CNTs have an outer diameter of ~15–40 nm. It was found that the present technique gives a higher yield and a high density of ACNTs bundles. Graphitisation of these CNTs is fairly good and the presence of catalyst particles in as-grown CNTs is almost negligible.

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