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# Synthesis of Aligned Carbon Nanotubes by Floating Catalyst Method Using Ferrocene

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**Abstract**

The aligned carbon nanotubes (CNTs) have been synthesised by floating catalyst method using ferrocene as catalyst precursor and acetylene as carbon precursor. The reaction was carried out at 850°C in double stage chemical vapor deposition (CVD) apparatus. The grown aligned CNTs were purified by air oxidation and acid treatment method. The aligned CNTs were characterised by using scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. The purity of CNTs was determined by Thermal analysis and X-ray diffraction method. The average diameter of aligned CNTs were around 20nm. This process not only produces aligned CNTs but also avoids the preparation of metal catalyst. The advantage of this method is simple and use of low cost precursors to produce high purity aligned CNTs.

**Keywords:** Aligned carbon nanotubes, floating catalyst method, ferrocene, double stage CVD

## Introduction

Since the discovery in 1991,[1] carbon nanotubes (CNTs) have attracted much attention due to their outstanding mechanical and electronic properties. CNTs are potential candidates for many applications such as field emission devices,[2] bio sensors,[3] chemical sensors,[4] hydrogen storage,[5] nanoelectronics,[6] catalyst support[7] and in composities as mechanical reinforcing agents.[8] Among the variety of synthesis techniques for CNTs, chemical vapor deposition (CVD) is the most suitable method for large scale production because of its low deposition, low cost and scalability. The introduction of a catalyst divides CVD methods into floating catalyst methods group, using a catalyst in the gas phase and fixed catalyst methods group with supported catalyst. The main advantage of floatingcatalyst method is that it does not require the stage of catalyst preparation as in the case of fixed catalyst method because the catalyst particles are continuously formed in the reactor and catalyst deactivation problem is avoided. Aligned CNTs have its own applications in spintronic devices,[9] microwave amplifiers,[10] field emission devices in flat displays[11] etc. So the synthesis of aligned CNTs with good alignment and purity is of great importance. Andrews *et al*. [12] obtained aligned CNTs by catalytic decomposition of ferrocene:xylene mixture. Ren *et al*.[13] synthesised aligned CNTs by plasma enhanced hot filament chemical vapor deposition. However, still the synthesis of aligned carbon nanotubes of high purity is still a big challenge for researchers.

In this paper, we wish to report the use of ferrocene and acetylene to synthesise aligned CNTs by floating catalyst method. The long aligned CNTs were grown by using double stage CVD at 850°C at gas flow rate of 15 sccm acetylene:600 sccm argon. The purification was done to remove catalytic

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particles by acid treatment method and by air oxidation method to remove amorphous carbon. The structural characteristics were examined by using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and laser Raman spectroscopy (LSR). The purity of CNTs was determined by thermal analysis and X-ray diffraction (XRD) studies. The advantage of this synthesis method is it avoids the catalyst preparation step and it can be transformed to continuous process.

## Materials and Experimental Procedures

The apparatus Figure 1 consists of two stage furnaces system fitted with quartz tube (25 mm Inner Diameter, 1200mm Length). Acetylene gas was used as carbon precursor and argon gas was used as carrier gas. 100 mg of ferrocene was taken in the quartz boat and placed inside the first heating furnace. Ferrocene was vaporised at 230°C and carried by argon flow (600sccm) to the second heating furnace after the temperature reached to 850°C. Acetylene gas flow (15 sccm) was allowed for 10 min. Finally, the furnace was cooled to room temperature in the argon flow. Carbonaceous material was deposited as a black film onto the walls of quartz tube, which was collected.

The as grown product contains iron nanoparticles which were removed by an acid treatment with HCl 5N at 80°C for 30 min. To eliminate the acid, finally the samples were washed with distilled water. The samples were dried in an oven at 100°C. The acid purified samples were again purified by air oxidation method to remove amorphous carbon.

The microstructure of the samples were obtained by using scanning electron microscope (SEM, SUPRA 40VP Carl Zeiss) and transmission electron microscope (TEM, CM200 Philips). The relative intensities of D-band and G-band were obtained by Raman spectroscopy (Renishaw, RM 1000, He-Ne laser excitation line at 633.0 nm). The as grown and purified samples were analysed by X-ray diffraction method (XRD, JEOL JDX 8P diffractometer with Cu Kα radiation, λ=1.5418A˚) to determine the purity of sample. The samples were again characterised by using Thermogravimetry (TGA, SDT Q600 TA) to determine the purity of sample after purification.

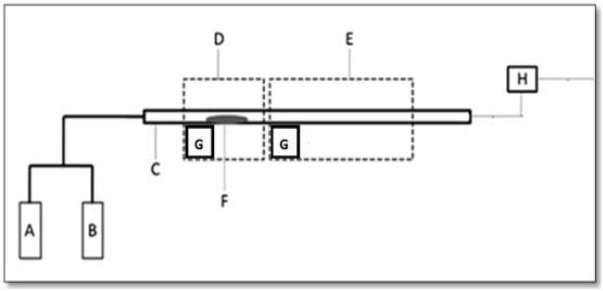


**Figure 1.** CVD set-up employed to synthesis aligned CNTs. A-Argon gas cylinder. B-Acetylene gas cylinder. C-Quartz tube. D - First heating furnace. E-Second heating furnace. F - Quartz boat. G-Controller. H- Water bubbler

## Results and Discussion

SEM images show the carpet like areas of aligned CNTs which were grown at 850 °C Figures 2. The length of aligned CNTs grown were of several micrometers. The formation of CNTs was further confirmed by TEM Figure 3. The TEM images clearly show the formation of well aligned CNTs of outer diameter around 20 nm. The TEM image also confirms the complete removal of catalyst particle and absence of amorphous carbon. Each CNT wall were made up of 20-30 graphitic sheets. The inner diameter of aligned CNTs varies form 5-10 nm.

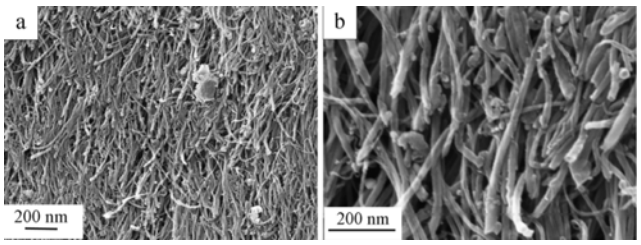


**Figure 2.** SEM Images (a) Low magnification (b) High magnification of grown aligned CNTs

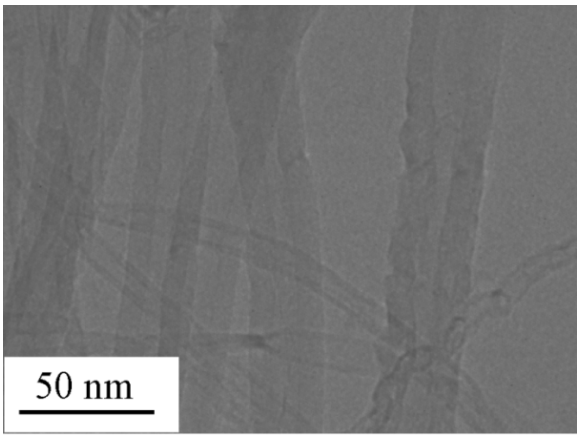


**Figure 3.** TEM Images of grown aligned CNTs

The Raman spectra obtained from aligned CNTs have shown in the figure 4. Spectra show 2 bands at around 1325 $cm^{-1}$ (D-band) and 1575$cm^{-1}$ (G-band). The D-band is due to disordered structure and the G-band is due to the graphitic structure of CNTs.[14] The $I_D/I_G$ value for the aligned CNTs grown is more than unity indicating the presence of defects in the structure.

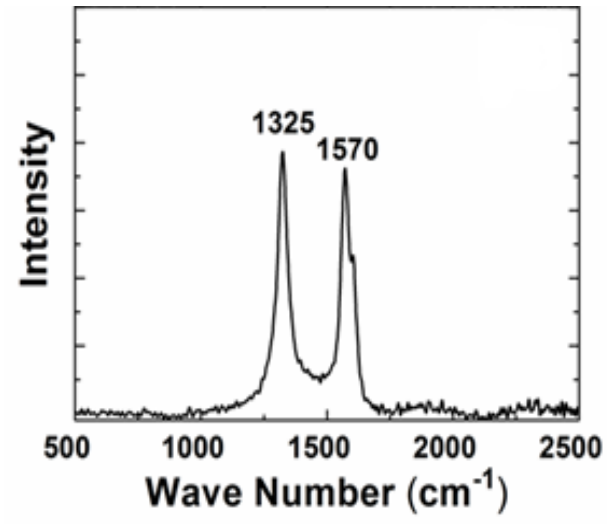


**Figure 4.** Raman spectra of grown aligned CNTs

In order to estimate the purity of the sample, TGA was performed in air. Figure 5 shows the TGA profile of as grown and purified sample. The TGA of as grown sample clearly indicates the presence of negligible amount of amorphous carbon and iron content impurities. The TGA of purified sample clearly shows the absence of amorphous carbon and only 1% of iron content was present which was unable to remove from acid treatment. The purity of the sample was again analysed by XRD. The XRD pattern (Figure 7) of as grown sample contains impurity (catalyst) peaks along with characteristic peaks of graphite. XRD peak of purified sample contains only two characteristic peaks at 26.0° and 43.5°, indexed with 002 and 101 diffraction planes of hexagonal graphite (JCPDS card files, no 41-1487), respectively. No other noticeable peaks induced by catalyst can be observed in the XRD pattern of purified sample.

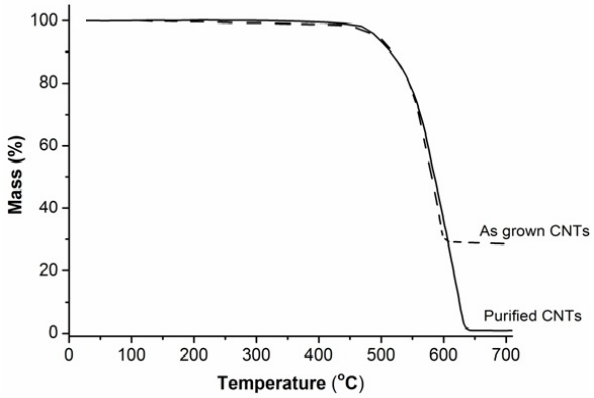


**Figure 5.** TGA analysis of as grown and purified aligned CNTs

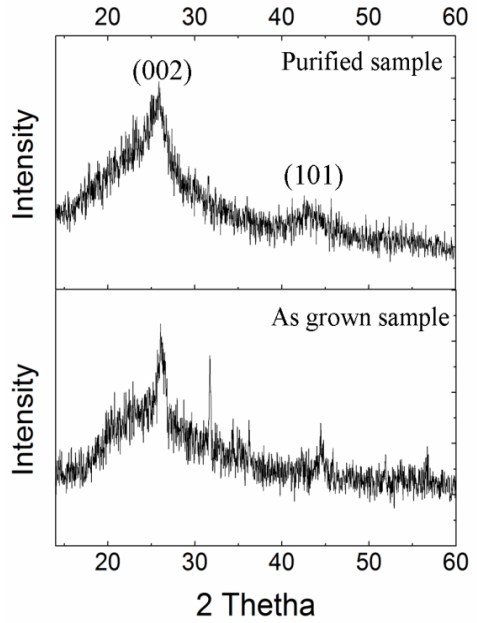


**Figure 6.** XRD peaks of as grown and purified sample grown

## Conclusions

Aligned CNTs have been synthesised by floating catalyst method using acetylene as carbon precursor and ferrocene as catalyst precursor. The diameter of aligned CNTs obtained were of around 20nm. The purity of purified sample was up to 99%. The advantage of this method is it avoids the catalyst preparation step and it can be transformed to continuous process.

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