

# Self-standing geometry of aligned carbon nanotubes with high surface area

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## Abstract

In this paper we report the development of self-standing tubular geometry of aligned carbon nanotubes with very high surface area ( $\sim 90 \text{ m}^2/\text{g}$ ). The synthesis involves spray pyrolysis of ferrocene-benzene solution in nitrogen atmosphere. The effects of temperature, ferrocene concentration, flow rate of nitrogen gas and the pumping rate of the liquid precursor were studied. The products were analyzed with transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Raman spectroscopy. The optimum condition for formation of macro-tubular geometry was found to be  $950 \text{ }^\circ\text{C}$ ,  $50 \text{ mg/ml}$  ferrocene in benzene,  $1.5 \text{ ml/min}$  pumping rate of liquid precursor and  $5 \text{ lpm}$  of nitrogen gas flow rate. The length and the diameter of the macrotube were  $5 \text{ cm}$  and  $1 \text{ cm}$  respectively with a thickness of  $120 \text{ }\mu\text{m}$ . The authors intend to use this tube in separation technology.

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## 1. Introduction

Since the discovery of carbon nanotube (CNT) [1], studies on its potential applications have been intense due to its unique properties. Some of the promising applications of CNTs have been as electrodes for electrochemical double layer capacitors, field emitters, nanoelectronic devices, for hydrogen storage, in composite materials etc. [2–6]. The recent years brought impressive breakthroughs towards application of CNTs in separation science and technology. The potential of carbon nanotubes (CNTs) in the removal of arsenic, fluoride, heavy metals and organic contaminants was examined by different researchers around the world [7–11]. The enhancement of the performance of the same by suitable functionalizations was also cited [9]. The fabrication of nanotube membranes with its applications has been discussed by Srivastava et al. [12].

Looking at the impressive credentials of CNTs and to make use of the potential benefits thereof, the authors aimed at producing self-standing geometry of CNTs with high surface area, which can serve as an essential aid to the membrane purification devices. For this purpose chemical vapour deposition (CVD) is the most suitable method, which is inexpensive and can be easily scaled up for continuous or semi-continuous production [13–15]. In this paper we report the synthesis of the self-standing tubular geometry of CNT with high surface area (one of the highest reported so far) and the optimization of the same.

## 2. Experimental

Different sets of carbon nanotube (CNT) were synthesized by spray pyrolysis process, which is a special kind of chemical vapour deposition. Ferrocene and benzene were used as the catalyst and carbon precursor respectively for the growth of CNT. The experimental setup is shown in Fig. 1. It consists of a sprayer, a container for the liquid precursor and a quartz tube (inner diameter  $10 \text{ mm}$ ). The sprayer is made up of a pyrex nozzle (inner diameter  $0.4 \text{ mm}$ ) and an outer pyrex tube with an exit diameter of  $2 \text{ mm}$ . The inner pyrex nozzle carries the liquid

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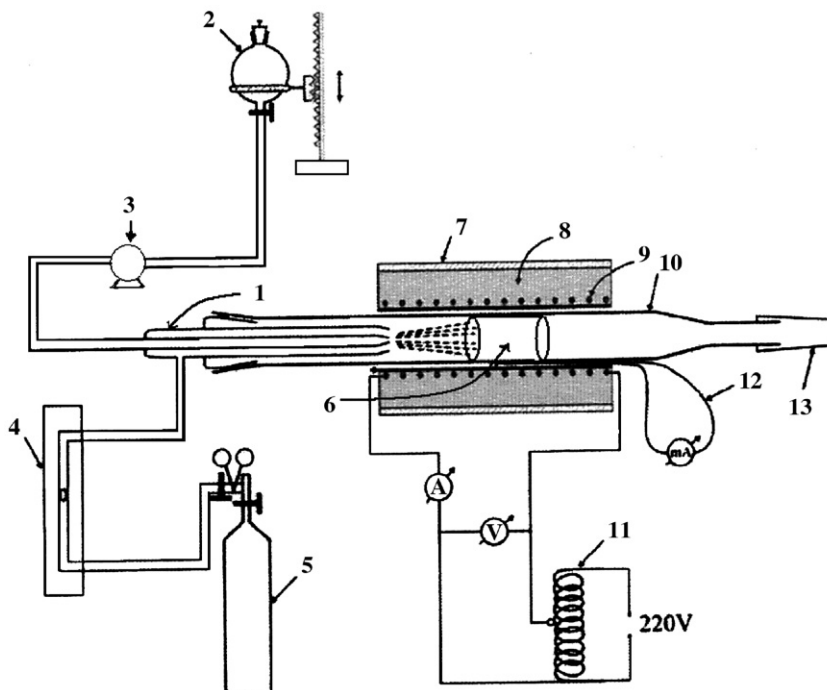


Fig. 1. Schematic of the spray pyrolysis set up. (1) pyrex sprayer (2) container for ferrocene-benzene solution (3) peristaltic pump (4) nitrogen gas flow meter (5) nitrogen gas cylinder (6) quartz template (7) furnace outer shell (8) thermal and electrical insulation (9) heating element (10) quartz tube (11) power supply (12) thermocouple (13) outlet to exhaust.

precursor and the outer pyrex tube carries the nitrogen gas. The sprayer is attached to the quartz tube, which is kept inside a resistant heating furnace. Ferrocene was dissolved in benzene and was pumped at the required rate into the spray nozzle by a peristaltic pump. Nitrogen gas was passed at a high velocity to convert the benzene droplets into spray and also to protect the CNT from oxidation at the temperature of synthesis. A quartz template of diameter 1 cm and length 5 cm was used to grow the macrotube architecture made up of CNT grown in the radial direction. Four parameters at three different levels, namely, temperatures of synthesis (750, 850 and 950 °C), concentration of ferrocene in benzene (30, 50 and 70 mg/ml), pumping rate of the feed benzene solution containing the catalyst (0.5, 1.0 and 1.5 ml/min) and the flowrate of nitrogen (5, 8 and 10 lpm) were varied to find out the effect on the morphology and growth of CNT.

After each experiment the quartz template was dissolved in hydrofluoric acid to get the carbon deposit grown over it. After filtering and washing with distilled water the carbon deposits were characterized by scanning electron microscopy (SEM VEGA MV2300T/40), transmission electron microscopy (TEM-JEOL, 200 kV) and Raman spectroscopy (ISA make). The specific surface area of the nanotube was determined using Sorptomatic 1990 instrument.

### 3. Results and discussions

The aligned CNTs were obtained in many cases; but self-standing tubular architecture with CNTs aligned in the radial direction was obtained only with the following process parameters: 950 °C of temperature, 50 mg/ml of ferrocene in benzene, 1.5 ml/min of pumping

rate of solution and 5 lpm of nitrogen flow rate. The macrotube of diameter 1 mm and length around 5 cm is shown in Fig. 2a. Fig. 2b shows the scanning electron micrograph (SEM) of the CNTs obtained at this optimum condition.

From the SEM the thickness of the macrotube was found out to be around 120  $\mu\text{m}$ . It was observed that the alignment could not be obtained at 750 °C, whereas higher temperatures (850 and 950 °C) promoted alignment. The higher pumping rate is helpful for the growth and yield of the CNTs as continuous supply of precursor and catalyst is obtained. The concentration of the catalyst plays an interesting role. At low concentration the yield is less. At high concentration the catalyst particles coalesce together and ultimately yield other nanostructured form (like nanoballs) along with nanotubes. In some cases though the temperature was high, low pumping rate and higher concentration of ferrocene yielded non-aligned CNTs. Very high flow rate of nitrogen destroys the alignment of CNTs. The specific surface area of these aligned CNTs was in the range of 89–94  $\text{m}^2/\text{g}$ , which is one of the highest so far reported for multi-walled aligned nanotube mass. The adsorption curve for the macrotube (Fig. 3a) reflects the microporous nature of the sample. The pore size (Fig. 3b) shows a bimodal distribution with a pore specific volume 0.22  $\text{cm}^3/\text{g}$ .

The Raman spectrograph of the macrotube (Fig. 3c) shows two peaks namely 'D' peak and 'G' peak. The 'G' peak at  $\sim 1580 \text{ cm}^{-1}$  corresponds to zone center vibrational mode of  $E_{2g}$  symmetry and the 'D' peak at  $\sim 1355 \text{ cm}^{-1}$  originates from the disorder in the graphene plane, corresponding to the  $A_{1g}$  mode of vibration [16]. The 'G' peak is very sharp and the ratio of 'G' peak and 'D' peak ( $I_G/I_D$ ) is around 2.03. This indicates that the CNTs are well graphitised.

At this optimum condition, the ferrocene-benzene droplets hit the hot surface of the quartz template and form a pattern of the Fe catalysts on the wall. Benzene gets decomposed and carbon species are dissolved in the Fe nanoparticles. These carbon atoms after getting

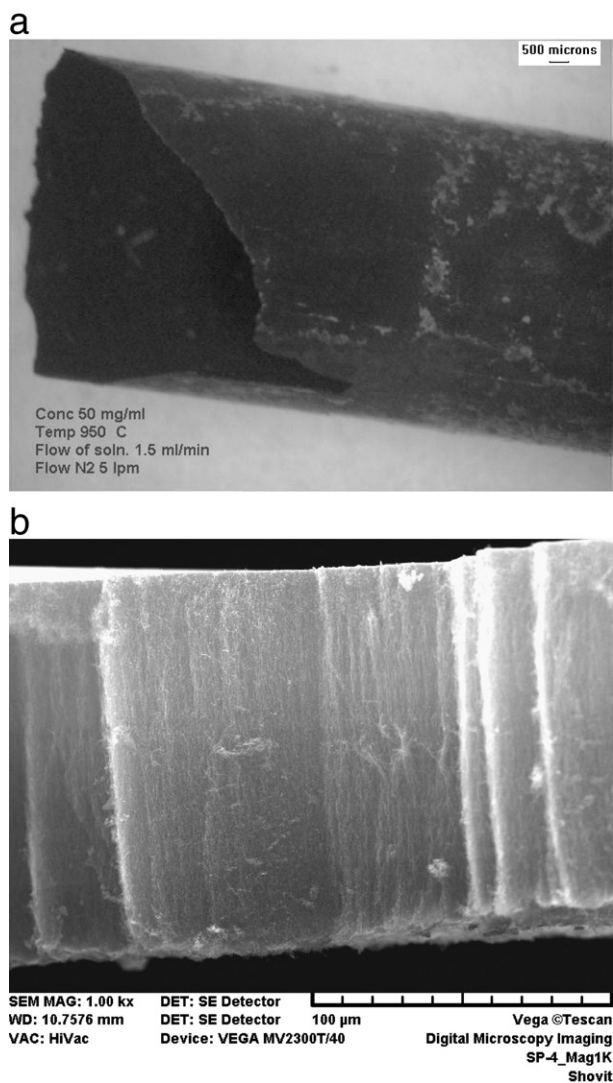


Fig. 2. (a) The stereoscopic micrograph of the self-standing tube made up of carbon nanotube. (b) SEM image of the self-standing tube showing the alignment of CNT in the radial direction.

supersaturated come out in the tubular form, which is the minimum energy configuration. The continuous supply of the carbon species result in axial and radial growth of the tube. The high pumping rate of the solution helps in growing longer tubes. The liquid droplet size produced by the nozzle decreases with increasing pumping rate and this produces larger tube with smaller diameter. Tapaszto et al. also suggested that the alignment of the tubes increases with increasing pumping rate of the solution [17]. The TEM image of the nanotubes (Fig. 4) obtained under the optimum condition shows a bimodal distribution of diameter with typical outer diameters 20 and 40 nm. Similar type of distribution was reported by Singh et al. [18]. The TEM image also shows partial filling of the nanotubes by the catalyst particles. For the growth of the self-standing macrotube dense packing of the nanotubes with sufficient length (in the radial direction of the macrotube) is required. The packing becomes efficient with the bimodal distribution of the diameter of the nanotubes. The partial filling of catalyst particles also helps in imparting strength to the macrostructure. This macrotube with such high surface area and bimodal distribution of pores is very useful for separation technology

as verified from our simulation studies (manuscript under preparation). The studies on the potential use of this self-standing tube in water purification are underway. It is planned to assemble these macrotubes

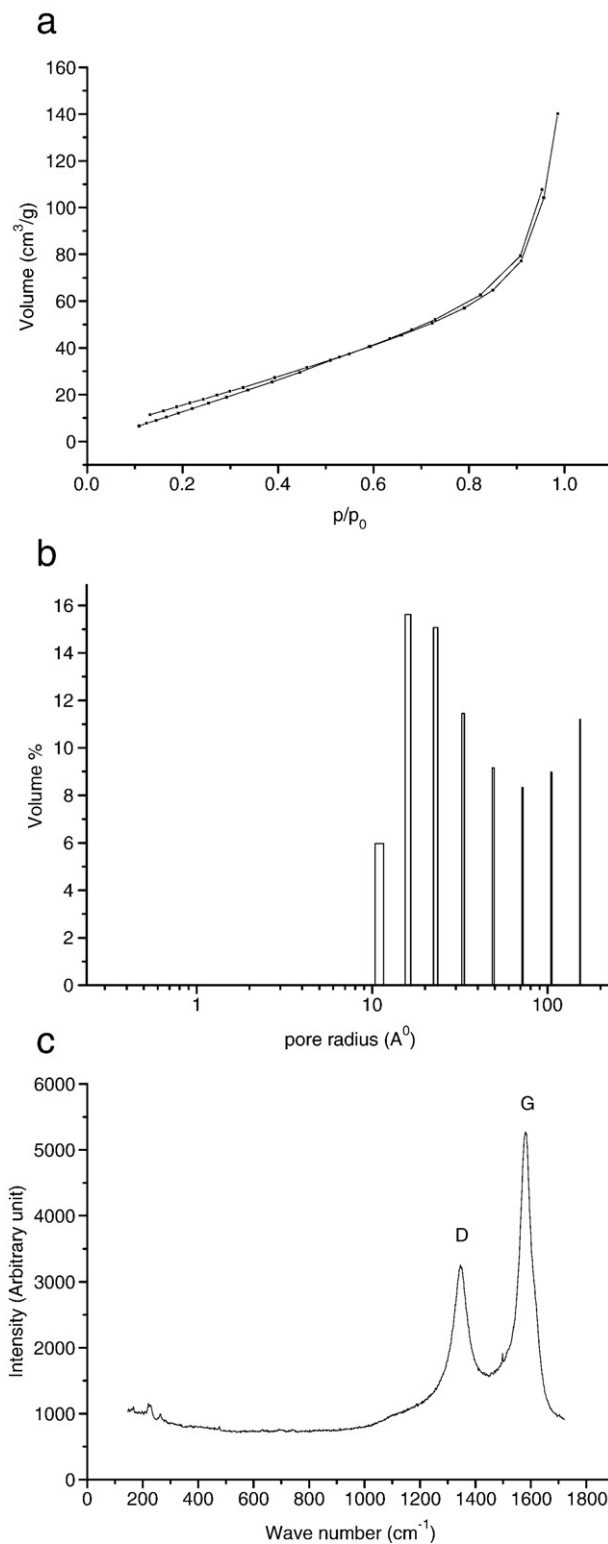


Fig. 3. (a) Adsorption/desorption isotherm of the self-standing tube showing microporous nature. (b) pore size distribution of the self-standing tube showing bimodal distribution. (c) Raman shift for CNT self-standing structure. The sharp 'G' peak and high  $I_G/I_D$  represent well graphitised sample.

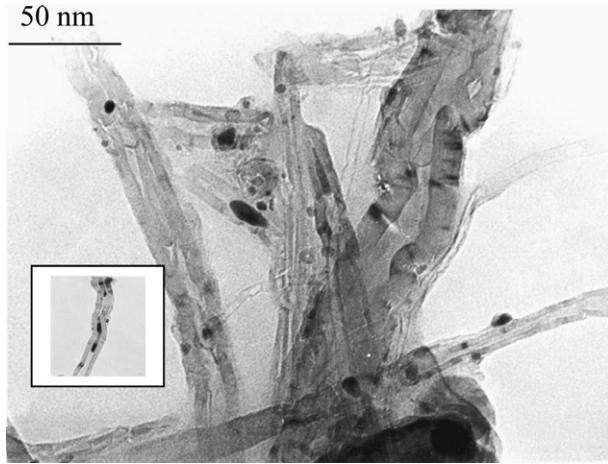


Fig. 4. TEM image of CNT sample showing bimodal distribution of diameter (average 20 and 40 nm). The inset image shows the partial filling of catalysts inside the tube.

in a metallic or ceramic shell to come out with an easily deployable filter-design.

#### 4. Conclusion

We developed a freestanding tube of CNTs, which is a great technological challenge. Spray pyrolysis is an efficient and essentially cost effective route for fabrication of such geometry. In this tube the CNTs are aligned radially. The optimum condition for formation of macro-tubular geometry was found out to be 950 °C, 50 mg/ml ferrocene in benzene, 1.5 ml/min pumping rate of liquid precursor and 5 lpm of nitrogen gas flow rate. The length and the diameter of the macrotube were 5 cm and 1 cm respectively with a thickness of 120 μm. The TEM

image showed bimodal distribution of diameter, which helped in dense packing of the nanotubes. The surface area of the tube is around 90 m<sup>2</sup>/g, which is one of the highest reported so far for such geometry.

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