Simple Fabrication of Carbon Nanotubes from Ethanol using an Ultrasonic Spray Pyrolysis

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Abstract. Carbon nanotubes of diameter (20–100 nm) are synthesized by pyrolyzing a sprayed solution of $Fe(C_5H_5)_2$ and C_2H_5OH in an Ar atmosphere at relatively low temperatures (around 800 ^oC). The tubular structures consist of highly crystalline nested graphene cylinders (<200 concentric tubes). Tube diameter can be controlled by varying the furnace temperature, carrier gas flow rate and the Fe:C ratio within the precursor solution. This low cost route for the synthesis of carbon nanotubes is advantageous due the low pyrolytic temperature, safety, processable in atmospheric pressure, and scalable.

Keywords: *carbon nanotubes/nanofibers; spray pyrolysis; ultrasonic nebulizer.*

1 Introduction

Since the first observation of carbon nanotubes (CNTs) in 1991,[1] extensive research has been focused upon the synthesis of CNTs because it is known for their unique electronic and physical properties. These features make them good candidates for potential applications such as hydrogen storage,[2] field emission,[3] and memory devices[4,5] amongst others.

In general, the synthesis of CNTs are produced by arc discharge,[6,7] chemical vapor deposition (CVD),[8,9] laser ablation,[10,11] etc. CVD-grown tubes, obtained by the decomposition of hydrocarbons in the presence of metal catalysts, are usually longer and can grow aligned if a patterned substrate is used as a catalyst.[3,12,13] However, one of the disadvantages in most CVD approaches reported hitherto is the use of toxic and hazardous gases such as C_2H_2, $FeCO_5$, etc., as the source of carbon.[14-17]

In this paper, we report the formation of carbon nanotubes/nanofibers [with outer diameter (o.d.)<100 nm; 250 μm long] at relatively low temperatures (around 800°C). This synthetic route involves the ultrasonic spray pyrolysis of ferrocene [$Fe(C_5H_5)_2$]/ethanol (C_2H_5OH) solutions in an Ar atmosphere. The advantages of this single-step process are: (1) the absence of both a prepatterned

catalytic substrate and hydrogen as a carrier gas; (2) the comparatively low pyrolytic temperature, and (3) the simple setup, and (4) the absence of vacuum conditions. Preparation of CNTs using ethanol has also been reported by Maruyama et al,[18] however, the processes were performed under vacuum conditions.

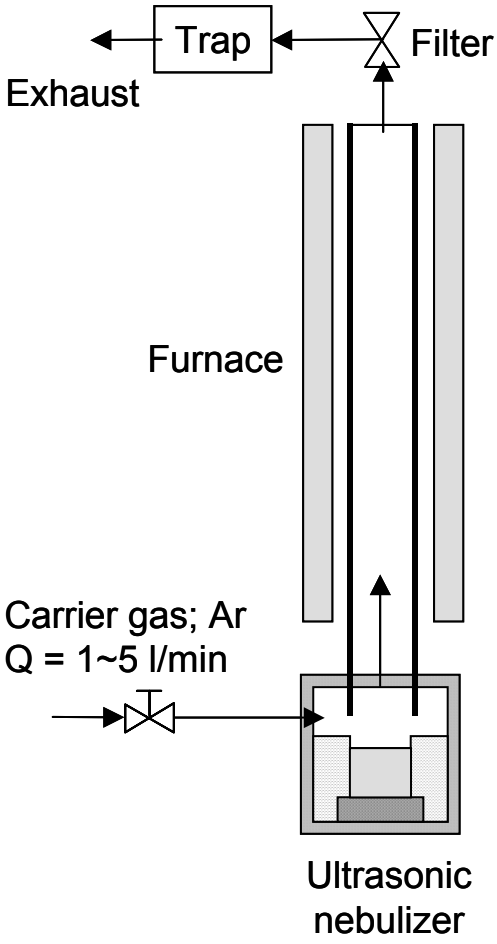

Figure 1 Schematic of spray pyrolysis equipment for production CNT.

2 Experiment

The spray pyrolysis setup consists of an ultrasonic nebulizer [1.7 MHz, Omron] and a quartz tube furnace [10 mm in inner diameter and 1 m in length]. The ultrasonic nebulizer is fixed to a tube furnace (Fig. 1). The precursor was ferrocene/ethanol solutions at various weight ratios. Argon (99.999%) was used

as a carrier gas to feed the sprayed droplet into the reaction tube, although other carrier gases can also be used. The reaction tube was heated to temperatures between 700 and 950 °C. The spraying period was varied between 15 and 60 min, depending on the precursor volume. The tube was maintained at the set temperature for additional 10 min in order to anneal the products. Various pyrolysis conditions (furnace temperature, Ar flow rate and the ferrocene/ethanol ratio of the solution) were carried out to explore their effects on the product.

The soot was deposited on the walls of the tube was analyzed by SEM (Hitachi S-5000; operated at 25 keV). The products were sonicated in acetone for 15 min and a few drops of the resulting suspension were transferred onto a lacey carbon grid for TEM observations (HR-TEM; HITCHI HF-2000) instrument.

3 Results and Discussion

Figure 2-4 illustrates the typical carbon nanotubes (CNTs) synthesized by the present method. From the morphologies and appearances, the diameters of CNTs are located in the range between 20-100 nm, so far similar to those synthesized by other methods. However the synthesis conditions reported here are significantly different. In the present method, the CNTs were formed and grown naturally in an atmosphere pressure, instead of vacuum as in the arc-discharge method and in the H_2 reducing agent as in the CVD and pyrolysis methods. In addition, no seeding materials—catalyze—were exteriorly added, whereas catalyze particles are indispensable when using other methods.

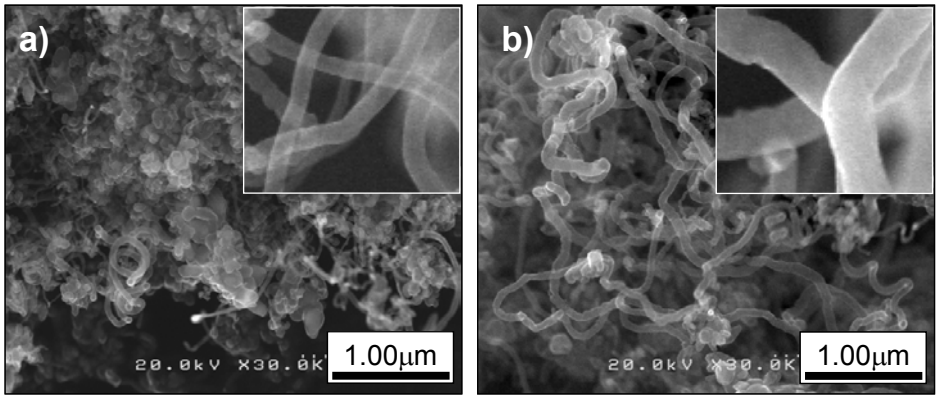

Figure 2 Effect of Fe:C concentration ratio on the prepared materials. a) 0.75 wt% and b) 1.5 wt%. The preparation temperature was 850 ^{o}C and gass flow rate was 2.0 L/min.

Figure 2a shows the SEM photograph of CNTs obtained at 850 °C using a ferrocene/ethanol ratio 0.75 wt% at the flow rate of 2 L/min of 100 ml solution. The CNTs diameters were about 40 nm (can be clearly seen in the inset of Fog. 2a). We produced samples at various ferrocene/ethanol ratios to investigate the effect of this ratio on the tube morphology. In general, we observed the tube diameter as well as the amount of the produced tubes increased with increasing the ratio of ferrocene/ethanol. As illustration, in Fig. 2b we show the sample prepared at ferrocene/ethanol ratio of 1.5 wt% (other synthesis parameters were maintained). The tube diameter increased up to 100 nm (see inset of Fig. 2b). By comparing Fig. 2a and 2b, it is clear that the amount of tube in Fig. 2a is higher that in Fig. 2a. It suggests that ferrocene/ethanol ratio controls both tube sizes and the amount of product.

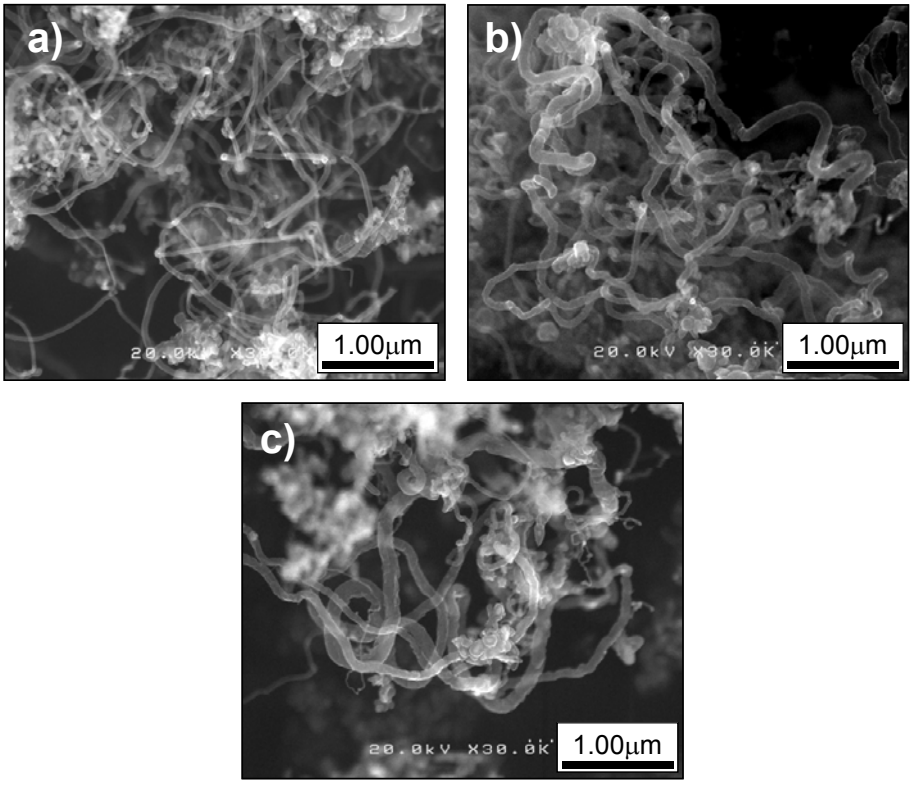

Figure 3 Effect of temperature on the prepared nanotubes. a) 800°C, b) 850°C and c) 900°C. The ratio of ferrocene/ethanol was kept at 1.5 wt% and gas flow rate at 2.0 L/min

The temperature of the furnace also affects the tube morphology. We tried various preparation temperatures from 700 °C up to 950 °C. The ratio of

ferrocene/ethanol was kept at 1.5 wt% and gas flow rate was 2.0 L/min. We were unsuccessful to produce tubes at temperatures below 750 ^{o}C. We only obtained shapeless carbon materials at temperatures below 750 ^{o}C. Figure 3 is the SEM images of samples prepared at (a) 800 ^{o}C, (b) 850 ^{o}C, and (c) 900 ^{o}C. At 800 ^{o}C, relatively long tubes were obtained. Increasing the preparation temperature up to 900 ^{o}C, increased the tube diameter. Further increasing the preparation temperatures above 950 °C resulted in the formation of carbon fibers (<100 nm o.d.) having noncylindrical shapes and highly disordered morphologies. Similar morphology was also reported by others.[10,12] This phenomenon could not be understood yet. The possible reason is the occurrence of ethanol fragmentation in the reaction zone at elevated temperatures (molecule decomposes at 1100–1200 ^{o}C).

Unsuccessful in producing tubes at higher preparation temperatures (above 950 ^{o}C) was also observed at other liquid consumption rates (adjusted by gas flow rates). Reducing the liquid consumption rate resulted in coating of the quartz tube with a thin layer of Fe, which rapidly oxidized into Fe2O3 when contacted with air.

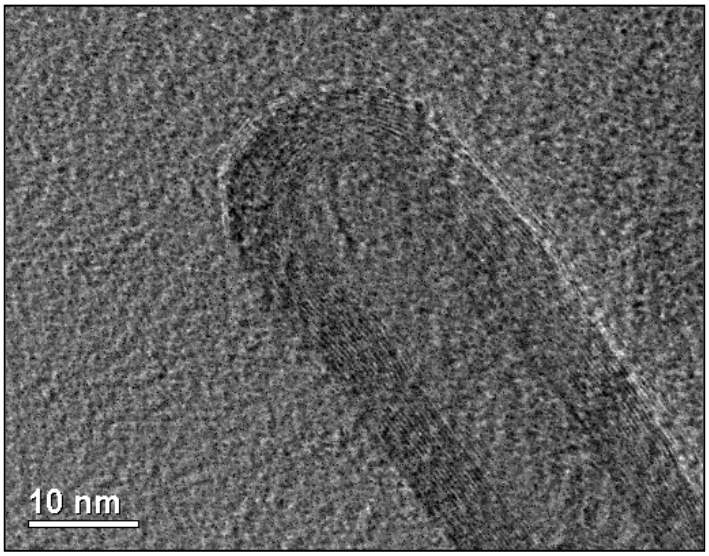

Figure 4 An example of TEM picture of a CNT prepared at temperature of 850 ^{o}C, ferrocene/ethanol ration of 1.5 wt% and gas flow rate of 2.0 L/min.

Figure 4 shows the TEM pictures of prepared tubes prepared at ferrocene/ethanol ratio of 1.5 wt%, temperature of 850 ^{o}C, and liquid flow rate of 2.0 L/min. The produced CNTs are multi-walled carbon nanotubes

(MWCNTs). The tube exhibits ~150 concentric graphene cylinders for which the straight fringes indicate a high degree of crystallinity.

Although the present method succeeded in producing CNTs in a very simple route, however, the morphologies of the produced sample are not so good when compared to those produced by other methods. Therefore, further investigations are needed to search the optimum preparation conditions so that the morphology of the produced sample can compete that of produced by other methods. However, allowing the CNTs to be produced in a very short time (several minutes) from spraying of the precursor until collection of the product by using simple equipment is a key potential of the present method. It is potential for production of CNT in a high quantity for use in various industrial applications. It is well known that spray methods have been applied in various industries such as foods, pharmaceuticals, cosmetics, pigments, paints, etc. to produce powder materials in a large scale.

4 Conclusion

Ultrasonic spray pyrolysis is a potential method for producing MWCNTs at relatively low temperatures in an atmospheric pressure. The method is safe, rapid, and potential for production of CNTs in a high quantity. The optimum synthesis conditions were tube temperatures of 800–850 °C, ferrocene to ethanol ratio of 1.5 wt%, and gas flow rate of 2.0 L/min. Further investigations are still required so this method is able to produce single wallet CNTs as well as CNTs having morphology that compete that of CNTs produced by other methods.

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