CONTINUOUS PRODUCTION OF ALIGNED CARBON NANOTUBES

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Introduction

Multi-walled carbon nanotubes (MWNTs) have been synthesized via the catalytic pyrolysis of hydrocarbons by several research groups around the world[1]. The use of preformed substrates by some of these groups allowed them to produce aligned MWNTs which may find applications as field emitters, reinforcing elements in polymer composites, etc. [1]. Here we describe a simple, inexpensive method for producing bulk quantities of high purity MWNTs aligned normal to bare silica substrates from the catalytic decomposition of a ferrocene - xylene mixture at ~700 ° C. Our synthesis method operates at near-atmospheric pressure and moderate temperatures, and gives very high selectivity to multiwalled nanotubes.

Experimental details and discussion

In the process described here, ~1 at % of ferrocene dissolved in xylene is fed continuously into a two-stage tubular quartz reactor using a syringe pump[1]. The liquid feed is passed through a capillary tube and preheated to ~170 ° C prior to its entry into the furnace. At this temperature, a liquid droplet on exiting the capillary, is immediately volatized and swept into the reaction zone of the furnace (650 - 1000 ° C) by the argon gas. Various synthesis parameters, such as the furnace temperature, ferrocene-xylene feed rate, reaction time, and the argon flow rate were optimized to produce high purity aligned MWNTs (Table 1 in Ref. 1). After reaction, the preheater and the furnace were allowed to cool to room temperature in flowing argon. Quartz substrates were placed within the reactor tube prior to reaction to act as additional sites for nanotube growth. These substrates were weighed before and after reaction to determine the amount of nanotubes produced at different sites within the reactor. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of the nanotubes deposited on the quartz substrates allowed us to monitor the quality of MWNTs grown under different operating conditions. The walls of the reactor tube were also scraped clean of nanotube deposits and this material was also weighed. At all times, the reactor was operated at 1" of H_2O pressure above atmospheric pressure to ensure that no oxygen enters into the reactor.

At ~1000 ° C, a small amount of nanotube material was formed at the entrance of the furnace and most of the ferrocene-xylene feed was converted into amorphous carbon and deposited on the tube walls, the quartz substrates and the water cooled condenser. However, when the reaction was carried out at ~700 ° C, aligned MWNTs were produced with high selectivity within the furnace, at an estimated ~30% conversion efficiency of the carbons in the ferrocene-xylene mixture to MWNTs. Typical SEM images of MWNTs deposited on the quartz substrates are shown in Figs 1 and 2. During the growth process, individual MWNTs self-assemble to form arrays of aligned nanotubes and the degree of alignment can be inferred from the SEM image of the central region of the array (see Fig. 2). High resolution TEM images and microdiffraction patterns obtained on individual MWNTs confirm a high degree of structural order in the walls on the nanotube[1] .

In terms of the growth mechanism of carbon nanotubes, it seems inescapable that nanotube formation is a specific case or extension of what is already known, and that nanotubes are routinely formed in many systems (even under non-optimal conditions) and have simply been overlooked. A recent example is the occurrence of nanotubes at the core of vapor grown carbon fibers [2]. In these catalytic reaction systems, which generally are operated at temperatures up to ~ 1100 ° C, a distinction should be made between the carbon that

is formed by interaction with the metal and that which is co-produced. For high selectivity, it is important to confine the reaction envelope to the immediate vicinity of the metal surface. Carbon atoms or fragments are produced by the catalytic decomposition of the precursor on the metal, which may be in the form of a solid substrate, as a dispersion of particles on a nonmetallic substrate, or introduced as "floating" particles into the gas. Carbon can be extremely mobile on metal surfaces, and vice versa. Hence, carbon atoms can diffuse rapidly over and through the metal, driven by a temperature or concentration gradient, to a location where they assemble into an ordered structure. To minimize the incidence of reactions away from the metal, the rate of carbon production must be limited. This can be achieved through an appropriate selection of the precursor compound, its thermal stability, partial pressure, the catalytic activity of the metal, and the reaction temperature. Successful growth of MWNTs in our study indicates that ~1 at % loading of ferrocene in xylene provides sufficient catalyst surface and selectively seeds the growth of MWNTs. This fraction of

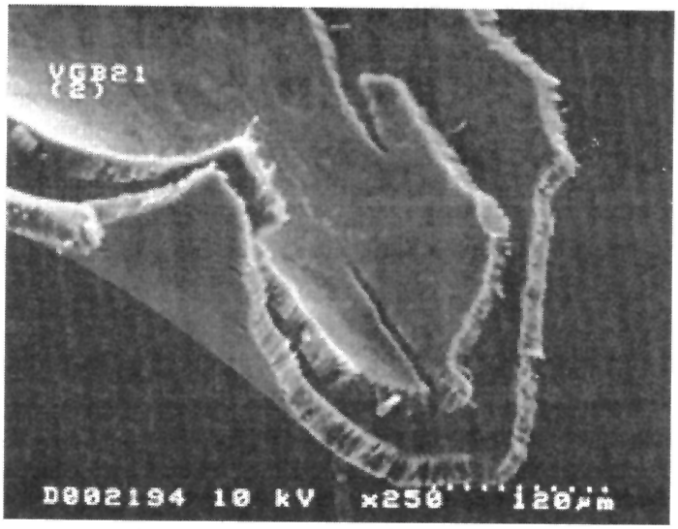

Fig. 1. SEM image of as-prepared MWNT array.

catalyst is consistent with the few at % used in the graphite targets or electrodes used in the pulsed laser vaporization [3] and the electric arc methods [4] of producing single walled carbon nanotubes.

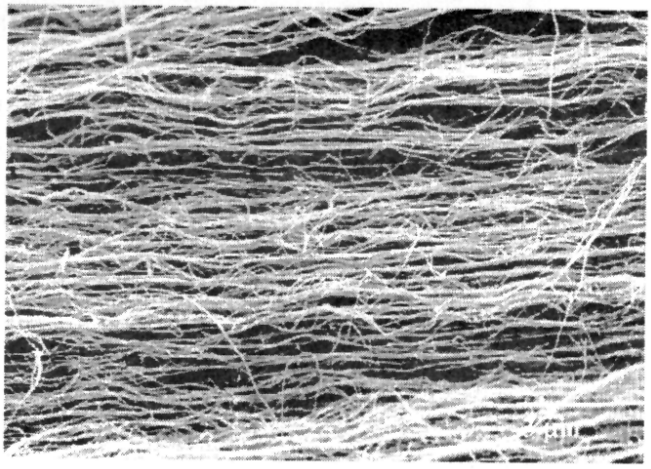

Fig. 2: Expanded SEM view of the central region of the array shown in Fig. 1.

In conclusion, it should be noted that our synthesis method to produce MWNTs could be scaled up and used for continuous or semi-continuous production. At a 30 % conversion efficiency of the total carbon feed to nanotubes, and the current cost of the materials used in our method, we estimate that carbon nanotubes could be produced at a cost of around tens of dollars per kilogram.

Acknowledgements

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References:

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