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A simple method for the continuous production of carbon nanotubes

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Abstract

A simplified arc-method is presented which allows for the *continuous* synthesis of multi-walled carbon nanotubes. In its basic form, the method requires only a dc power supply, a graphite electrode, and a container of liquid nitrogen with no need for pumps, seals, water-cooled vacuum chambers, or purge-gas handling systems. High-quality nanotubes are produced in high yield. The system is easily adaptable to produce large quantities of nanotubes continuously without interruptions for electrode replacement, chamber cleaning, or gas purging. © 2000 Elsevier Science B.V. All rights reserved.

Carbon nanotubes [1] have unique mechanical and electrical properties that make them attractive systems for fundamental scientific studies as well as for a wide range of applications including electron field emission sources [2–4], nanoscale electronic devices [5–8], chemical filters and storage systems [9], and mechanical reinforcements [10,11]. Various synthesis methods have been developed for the production of nanotubes, including carbon arc plasma growth [12–14], laser vaporization [15], and chemical vapor deposition (CVD) [16–18]. While these methods can produce high-quality nanotubes in yields suitable for limited research use, no method has been developed for the production of high-quality tubes which is continuous and easily adaptable to industrial production levels. The most common synthesis method is that of arc-plasma growth, which necessitates a liquid-cooled sealed chamber with special sliding or bellows seals for continuously-cooled electrodes, complex gas handling equipment [12,19], and time-consuming purge cycles. After each limited synthesis run, the chamber must be opened in order to extract the nanotube product. Laser vaporization methods suffer similar constraints. Even CVD methods, which hold some promise for scalability, necessitate cumbersome gas handling systems, high-temperature furnaces, and carefully prepared consumable substrate catalysts [18].

Here we describe a simplified carbon-arc nanotube synthesis method that eliminates nearly all of the complex and expensive machinery associated with conventional nanotube growth techniques. Indeed, all that is required is an insulated bucket full of liquid nitrogen, graphite electrodes, and a dc power supply. The reaction can run in a continuous fashion and can be scaled up for industrial production levels.

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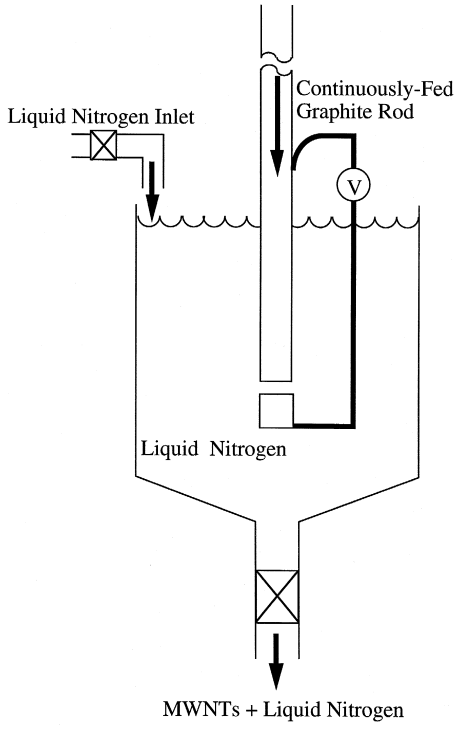

Fig. 1. Schematic of continuous production liquid-nitrogen reaction chamber for nanotube synthesis.

High-quality multi-walled carbon nanotubes are produced at high production rates.

Fig. 1 shows a schematic of the synthesis apparatus. To grow nanotubes, a graphite anode is dipped into an open container of liquid nitrogen containing a short non-consumable copper or graphite cathode. The electrodes are momentarily brought into contact and an arc is struck. Nanotubes formed in the arc-plasma region drop and collect on the bottom of the bucket. For continuous operation, the bottom of the bucket is funnel-shaped and sealed with a valve which opens automatically and periodically to flush nanotubes from the vessel. In this configuration, the graphite anode rods are threaded one into another and continuously fed through a simple sliding electrical contact. The level of liquid nitrogen in the insulated vessel is automatically maintained using a level sensor and fill pipe. This production scheme allows for nanotube synthesis at a 100% duty cycle.

The advantages of this simplified design are many. No gas purging is required, as the liquid nitrogen provides a protective (oxygen-free) environment as well as being the source of the buffer gas during the arcing process. The liquid nitrogen further maintains the necessary temperature gradient within the plasma. All complex vacuum seals are eliminated, including the typically troublesome sliding seals around the electrodes. Finally, the nanotube products (which have been shown to be extremely air-sensitive after synthesis [20,21]) are easily maintained and transported in an inert environment following production.

During operation of our prototype system using a 1/4" graphite anode and 1/2" graphite cathode, multi-walled nanotubes were produced using a dc current of 60 A at 20–25 V; the arc was extremely stable. The arc reaction consumed ~ 0.2 l of liquid nitrogen per minute of operation. The total yield of nanotube-rich material was 44 mg per minute per cm^2 of anode surface area, a comparable (per unit anode area) yield to that of an optimized conventional (but unscalable) arc reaction [12–14].

To characterize the nanotubes produced by our synthesis method, the raw nanotube-containing product was crushed and sprinkled onto transmission electron microscope (TEM) grids and imaged with a high-resolution TEM operating at 200 keV. Multi-walled nanotubes were omnipresent on the grids with high relative yield. Fig. 2 shows a representative

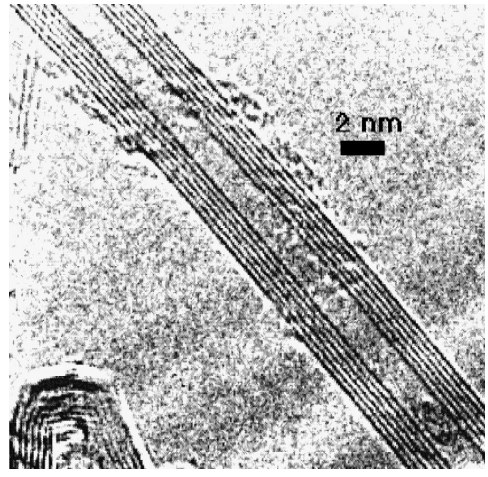

Fig. 2. High-resolution transmission electron microscope image of a multi-walled carbon nanotube produced by the liquid-nitrogen arc reaction method.

TEM micrograph of the nanotubes. In general, the nanotubes were of high quality with 4–8 layers and with long and straight parallel walls with only occasional surface contamination. In fact, the tubes grown using our liquid-nitrogen method appear to have consistently cleaner surfaces than tubes grown using other methods. We further characterized the stoichiometry of our nanotubes using electron energy loss spectroscopy (EELS) in the TEM. The tubes are composed only of carbon with no evidence for nitrogen incorporation.

A most important feature of this new synthesis method is that there appear no obvious cost or technology obstacles to scale the method up for high-quantity production. In addition, the method should lend itself well to the formation of different types of nanotubes (such as single-walled tubes and tubes containing non-carbon elements) by including catalytic particles such as cobalt and nickel [14,15] or other elements such as boron [22] in the anode.

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