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Continuous carbon nanotube production in underwater AC electric arc

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Abstract

A simple, low cost and continuous growth method for the production of well graphitized multi-wall carbon nanotubes is described. The growth takes place in an AC arc in water between two carbon electrodes. At a voltage of 40 V the arc is stable in the range of 85–45 A, lower current values help in increasing the fraction of carbon nanotubes in the product.

Carbon nanostructures are continuously in the focus of attention since their discovery [1] and the large scale production of fullerene material by a DC arc procedure [2]. Carbon nanotubes (CNT) discovered in 1991 by Iijima in fullerene soot [3], proved to be a class of carbon nanomaterials with very promising properties [4]. An extremely wide range of practical applications is foreseen from nanoelectronics [5] to chemical sensing on molecular scale [6], and lightweight composite materials with improved mechanical, thermal and electric properties [7]. One of the most serious bottlenecks in achieving these goals on an industrially significant scale, is the still very high cost of CNTs after a decade from their discovery. To overcome this, inexpensive, simple, and easily up-scalable production methods are needed, which do not involve vacuum equipment, extensive live labour, or low temperatures. Here we describe a method based on a computer controlled AC electric arc, which we believe, matches the above conditions.

Arc growth was the first method for the production of macroscopic amounts of multi-wall carbon nanotubes (MWCNTs) [8]. Most frequently the arc growth is carried out in low pressure He or other neutral atmosphere. Sealed reaction chambers and vacuum equipment are needed to provide this atmosphere [8,9]. On the other hand, opposite to catalytic tubes, the arc grown MWCNTs are known to be well graphitized [10]. Beyond the need for vacuum equipment another major problem of the conventional DC arc growth in low pressure neutral gas atmosphere is the need to interrupt the growth to remove the

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product from the growth chamber. The catalytic method [11] usually suffers from a similar drawback and additionally, the preparation of the catalyst is very labour intensive.

Recently a DC arc in water was reported as suitable way to produce carbon onions [12]. The growth of CNTs in a DC arc under liquid nitrogen [13] was reported, too. Unfortunately, the use of cryogenic temperatures is costly and not always desirable in industrial production. In a very recent paper a DC arc method was reported for the underwater growth of CNTs [14]. However, the potential benefits of working underwater were used only in part.

Surprisingly, the possible use of AC arcs got very little attention in CNT growth experiments. The effects arising from the use of an AC arc between two carbon electrodes of different diameters, in Ar atmosphere, were studied by Koprinarov et al. [15]. The major difference when using an AC power supply as compared with a DC arc is that vaporization of carbon atoms occurs in 'pulses' separated by the change of the polarity of the supply voltage.

In our procedure we combine the underwater growth with the use of an AC power supply and computer control. Furthermore, we try to benefit fully from the liquid environment and of the fact that the product is not formed on the electrodes. The deposition of the nanotubes on the cathode and their etching was reported as an inconvenience when using DC power, reducing the duration of a typical growth cycle to 2 min [14]. In our case there is no product found on the electrodes after the growth experiments, the deposit peels off the actual cathode in the next half cycle when the role of the electrodes is reversed. This makes very easy the removal of the product from the system without the need to stop the growth and avoids the etching of the grown nanotubes. Due to the above mentioned reasons the AC method is well suited for *continuous operation* and *automation*. Both are of crucial importance if industrial application is targeted.

An AC electric arc is generated between two identical carbon rods of 6 mm in diameter, submerged in deionized water. No special shaping of the electrodes was used. Two computer controlled stepper motors, like shown in the schematic drawing in Fig. 1B, are used to regulate the distance between the electrodes. The current was varied between 85 and 45 A, at a voltage of 40 V. For all settings it was possible to ignite and maintain the arc. The production rate of carbonaceous material is of the order of 5–10 mg/min, in case of the highest current of 85 A, it is higher than the one reported in [14]. The production rates, weight losses of electrodes and the proportion of them as a percentage of the weight loss of the electrodes for each current value is presented in Fig. 2. Gas bubbles are continuously formed during the arc discharging process in the water.

The product was investigated by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The three main constituents, Fig. 1D, are agglomerates of multi-wall carbon nanotubes and bucky-onion type structures (AMBs), soot, and graphitic particles. The proportion of nanotubes in AMBs can be estimated as about 50% from TEM investigation. In contrast to results reported for the underwater DC arc [12,14], from the AC plasma, especially, when the arc is operated at a low current, the main products were AMBs with at least 80%. At higher currents the proportion of graphitic particles and soot is higher and reaches the 50% at the highest, 85 A sample. The monotonous increase of the weight of the product as a percentage of the weight loss of the electrodes with the increasing current was observed, see Fig. 2. Carbon can leave the system in gaseous, oxidized form only so oxidative processes must be present regardless the value of used current. Oxygen is supplied by the electrolytic decomposition of water. The formation of gas bubbles was reported by Zhu et al. [14], too, they found CO and H_2 in the gas. These oxidative processes seem to be enhanced at lower currents, while at higher currents carbon appears favorably in elementary, solid forms (soot, graphite). The proportion of the electrode weight loss transformed into AMBs, can be calculated as 13% for the lowest and 18% for the highest current case, so the dependence of the AMB production on the arc discharge current value does not seem to be strong while the product quality shows a stronger dependence on the current used. This observation may be useful in future optimization experiments.

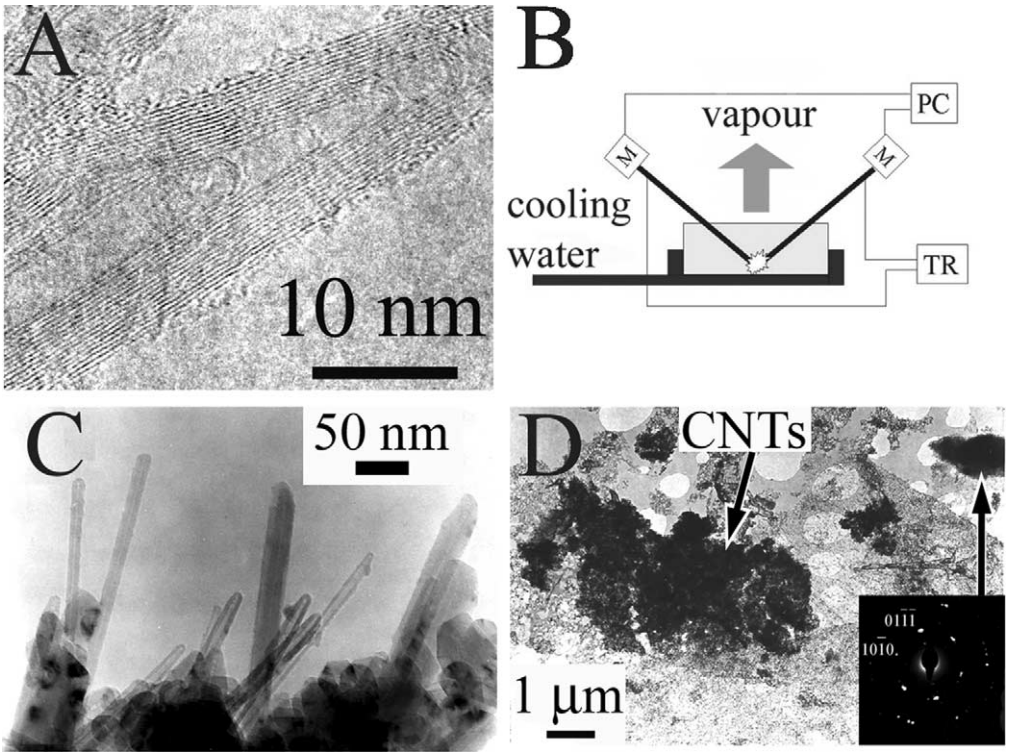

Fig. 1. Carbon nanotubes produced in an underwater AC electric arc. (A) HRTEM image showing multi-wall carbon nanotubes with well graphitized, straight walls and tapered ends. (B) Schematic presentation of the growth apparatus: M, stepper motors; TR, welding transformer; PC, computer. (C) TEM image showing straight multi-wall carbon nanotubes protruding from an agglomeration like the one shown in D. (D) The three main constituents of the arc product: agglomerates of multi-wall carbon nanotubes and bucky-onion type structures, soot and graphitic particles, electron diffraction is shown on one of the graphitic particles.

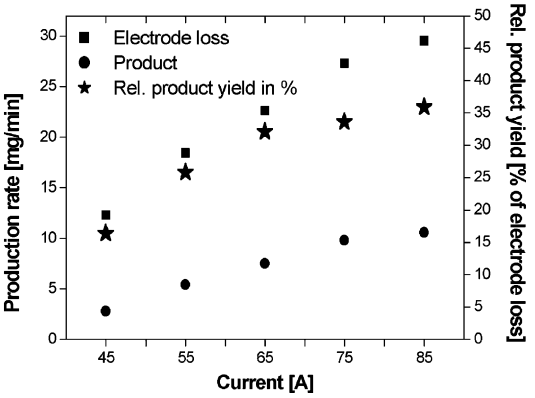

Fig. 2. The weight of the carbonaceous product, the weight loss of the electrodes and the relative yield of carbonaceous product, e.g. the weight of the product as a percentage of the weight loss of the electrodes.

The HRTEM images, Fig. 1A, show that the walls of the MWCNTs are well graphitized, similarly to vacuum-arc grown MWCNTs.

One hour isochronal annealing experiments were carried out in air at temperatures in the range of 450–700 °C using the sample produced with 65 A current. Only insignificant (a total of 8 wt%) weight loss occurred below 650 °C and 15 wt% was lost when the sample was annealed for 1 h at 650 °C. This is a strong indication that the proportion of disordered carbons in the sample is fairly low and the structural quality of the MWCNTs is high. As a comparison, under similar oxidation conditions the catalytically grown MWCNTs – which contain many structural imperfections – yield 40 wt% loss when annealed at 550 °C for 1 h.

Experiments were carried out with spectral pure carbon rods and with low-purity electrodes, as well

(used in old-fashioned movie apparatus). The growth can take place even in normal tap water. When working under low-purity conditions, in addition to the constituents shown in Fig. 1, disordered onion-like formations were also found. The morphological character and structural quality of nanotubes and bucky-onions as well as their proportion in the AMBs found in lower but still significant proportion was not different from the high-purity case. The product contained silicon, sulfur, calcium, iron and oxygen in small amounts besides the carbon. The exact amount of the impurities and their chemical composition was not determined, the influence of the different impurities, additives on the reaction and the product needs further investigations. On the other hand, the fact that no high-purity materials, opposite to [14] no catalyst and special shaping of electrodes (drilling or else) is needed, makes to production cheap enough to allow for oxidative purification by burning away the disordered forms of carbon.

We believe that this procedure is very well suited for scale-up and for continuous operation. High intensity AC is widely used in many industrial applications, e.g., like a welding apparatus used in our case to power the growth. The water can be used as a medium to prevent oxidation, to cool the reaction environment, and to help to remove the product. If a suitable filtration system is added, the procedure allows a low-cost continuous operation with minimal operator intervention needed (only to change the consumed electrodes). These together may lead to rapid spreading of the technique, making readily available good quality MWCNTs needed for industrial applications.

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