Letters to the Editor

Catalytic synthesis of carbon nanotubes under ion irradiation

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The discovery of carbon nanotubes (CNTs) [1] has motivated intense interest in the study of their peculiar structure, physical properties [2,3], synthesis method and formation mechanism [4–6], and the potential technological application [7]. It is common knowledge that the CNTs were prepared typically by a dc arc discharge method [8], laser vaporization of graphite [9] and chemical vapor deposition (CVD) [10]. Among these, the chemical method, namely, the catalytic method of decomposition of hydrocarbons and CO, are found to be promising in having a high yield of carbon nanotube production. In our previous work, the direct transformation of commercial graphite into carbon nanomaterials [11] and conical-shaped carbon nanotubes without any catalyst [12,13] have been accomplished. Indeed, these investigations led to the realization that it should be possible to synthesize CVD-like nanotubes if we adopt the double-ion implantation containing catalytic element (such as iron or other) ion. Therefore we decided to investigate the formation of CNT using Fe+ ion and subsequent Ar+ ion irradiation on the carbon plate surface. A quite surprising result which emerges from the double ion (catalytic ion and impacted ion) irradiation experiments is that CNTs are found on the surface of carbon target. This is also the first example of CVD-like nanotube growth by double-ion beam irradiation of carbon target. CNTs were prepared using the double ion successive irradiation. First, the carbon plate (containing amorphous carbon and some fine-grained graphite crystals) was implanted with 60keV Fe+ ions (dose: \(5 \times 10^{17} \text{ cm}^{-2}\)) at room temperature. Afterwards, as-implanted sample was implanted again with Ar+ ion under same conditions. The morphology of CNTs was characterized by a LEO-1530-VP field-emission scanning electron microscope (FE-SEM) with accelerating voltage of 10kV. The microstructures of the CNTs were studied with a Philips CM200 EFG model high-resolution transmission electron microscope (HR-TEM) operated at the accelerating voltage of 160kV. To prepare a TEM specimen, the material contained nanotubes taken from the ion-irradiated carbon target was glued directly onto a holey-carbon copper microgrid for TEM examinations.

Fig. 1 shows a top view SEM image of as-grown CNTs on the textured graphite surface irradiated by Fe+ followed by Ar+ (Fig. 1a). It is clear that nanotubes were randomly distributed on the surface of the textured carbon target. The nanotubes have an average diameter of 20 nm, and some of them cross each other. We find that the well-grown CNTs with or without Fe particle on their end are present in our samples. Further structural characterization of an individual CNT was carried out using TEM. High-resolution TEM images reveal that the nanotube is well graphitized and typically consists of 10–30 concentric graphite layers with the spacing of 0.34 nm between adjacent lattice planes. An interesting result is the tendency of graphite layer and

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of nanotube to partially bend and curve during growth (as see Fig. 1a inset). In general, the bending of graphite layers requires the introduction of defects such as pentagons or heptagons into the shells. These defects can indeed be created during growth of under ion irradiation [14]. In addition, extensive high-resolution TEM investigations did not reveal any single-walled CNT in our samples, possibly because the catalytic Fe particle sizes are too large to form SWCNTs [15]. Very interestingly, several kinds of the multi-walled carbon nanotubes (MWCNTs) with various morphologies and structures were observed:

1) Long CNTs, with lengths from 0.1 μm to several tens of microns, some of them have caped Fe catalyst particle partially exposed to environment (see Fig. 1b) which is similar to the nanotubes synthesized by catalytic CVD methods [16]. The fact that long CNTs observed here have their catalyst Fe particles partially exposed indicates that the direct contact of catalyst surface with carbon source is essential for continuous CNT growth during Ar+ ion irradiation. This probably is similar to the growth mechanism of catalytic carbon nanotubes proposed by Dai et al. [17]. These iron particles were forming in the carbon matrix and became partly exposed in the surface of the carbon target due to the irradiation. Then nanotubes were growing under the iron particles. So the bottom end of this CNT must be opened and should form a bowl-shape structure if this nanotube is stripped off from the matrix during TEM sample preparation.

2) CNTs with closed tips at both ends. As shown in Fig. 1c, the tips of these CNTs are all closed, and the majority of tips are not encapsulated with any catalytic particles. From high-resolution TEM images (see Fig. 2), it can be clearly found that the hollow cavity of the depicted nanotube is directly closed to become the capped end by the graphitic sheets. This reveals that the nanotube could grow even without a catalyst particle on the tip, because the carbon source for the further growth of nanotube may come from the direct deposition of carbon atoms on the open tip, which then transform into graphitic layers of nanotubes [11].

3) Stout CNTs. Fig. 3 is a TEM image of the morphologies of two typical stout nanotubes. One tip of the nanotube-A is not encapsulated with any catalytic particle, as indicated by arrow (1), which

Fig. 1. (a) SEM image of as-grown CNTs on the textured graphite surface by Fe+ + Ar+ irradiation in proper order. The inset shows a high-resolution TEM image of a typical nanotube. (b) A carbon nanotube tipped catalyst particle Fe indicated by arrow, which is grown on a textured graphite surface. (c) Several CNTs closed their tips at both ends.

Fig. 2. (a) and (b) HRTEM images showing two typical closed ends of a CNT without any catalytic particles on their tips.
would correspond to the root (see Fig. 3 left inset), while the image showed this nanotube-A terminating in a nanoparticle at the other tip as indicated by arrow (2). From nanotube-B (Fig. 3), we can see that its two tips are both capped with catalytic particles [see arrow (3) and arrow (4)]. Further TEM examinations show that the crystallinity of graphitic sheets (separated by $\sim 0.34\text{nm}$) is nearly perfect, though some parts of nanotubes are not straight, and not with uniform inner and outer diameters. In addition, there are Fe catalyst particles with different shapes in the cavities of the stout CNTs (see Fig. 3, indicated by arrows). Energy-dispersive X-ray (EDX) spectra taken from these nanoparticles show the presence of carbon, iron and a small amount of oxygen, which indicates that these particles are iron/carbon particles (not shown). The sizes (or lengths of column-like particles) of these particles and the distances between two adjacent particles in a nanotube body have no any regularity. This fact means that the nanotube maybe have different growth velocity during their growth process [16]. The growth velocity of a nanotube is also determined by ion irradiation characteristic features.

In addition, in a similar experiment (not shown here), TEM observation of the material collected in the surface of the carbon target just after the Fe$^+$ ion implantation using same conditions did not reveal any Fe/carbon nanoparticles, but a small amount of Fe element was present in the EDX pattern. Thus we cannot exclude the possibility that there exist very small clusters of Fe and/or Fe/carbon in those samples, because TEM has a minimum resolution limit of several Å. These symptoms indicate that during Fe$^+$ irradiation, the iron must be atomically dispersed or clustered to form a precursor for the growth of Fe-nanoparticles. Furthermore, during Ar$^+$ irradiation following Fe$^+$ irradiation, the Fe-cluster should aggregate into Fe-nanoparticle which is required to reach the suitable size and catalysis, and will thus results in the CVD-like nanotubes growth.

From observed and described above, we propose that the growth of the nanotubes by double ion irradiation with carbon target involved the combination of two processes, namely the catalytic ion (Fe$^+$) implantation and synthesis ion (Ar$^+$) bombardment. First, in the surface of carbon target, the implanted iron atom aggregated to form Fe-cluster which acts as a precursor for the formation of catalytic nanoparticles. Consequently, in the initial stage of Ar$^+$ bombardment, upon further aggregation, the catalytic Fe-particle would emerge, and, with the continual supply of ion-induced carbon source, various carbon nanotubes would form. However, it has been known that argon ion bombarded target is effective in etching carbon materials [14]. Thus, we believed that the ion etching rate and Fe particle catalytic efficiency (nanoparticle formation and chemical activity) are two competitive processes, that is, when the catalytic efficiency of a metal prevails, nanotubes are unambiguously formed. It is apparent in this study that the precipitation rate of carbon on the surface of Fe/carbon particles is faster than the etching rate of graphitic sheets. It also means that the nucleation and growth of carbon nanotubes can under double ion irradiation conditions be catalyzed efficiently by Fe/carbon nanoparticles.

The growth mechanism of various carbon nanotubes of the present time is not clearly understood. It is commonly believed that localizability in space and discontinuity in time caused by random injection of innumerable ions will result in a growth change of nanotube structure in site and time during growth process. A possible process for the formation of various carbon nanotubes in double ion irradiation is that, during irradiation of implanted-Fe samples, locally melted region in the center of the cascade occurs [18]. At the same time, the Fe/carbon nanoparticles could be formed in these regions. Thus, it can be inferred that if these conditions were present, it might leads to considerable carbon atom clustering and motion surrounding the nanoparticles, and that the presence of the Fe-nanoparticles can catalyze the carbon atoms and/or clusters transformation towards graphitic layers which encircle catalytic particle in a similar way, as in CCVD (catalytic chemical vapor deposition) nanotubes growth.

In summary, we successfully obtained various multi-walled carbon nanotubes (MWCNTs) including bent or
distorted nanotubes, using the double ion (Fe⁺ and Ar⁺) irradiation method. This approach is expected to form a new general route for synthesis of MWCNTs, the growth mechanism and physical properties of which are of great interest. This multi-ion irradiation idea may also be valid for other material and be used for fabricating nanostructures. For the present, we have no theoretical bases enabling us to interpret the growth mechanism of such CVD-like nanotubes. Further theoretical and experimental efforts are therefore required to understand this growth process of CVD-like nanotubes in detail.

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References


Separated syntheses of Gd-hybridized single-wall carbon nanohorns, single-wall nanotubes and multi-wall nanostructures by arc discharge in water with support of gas injection

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In the latest few years, ‘arc in liquid’ method [1–5] has been developed as a cost-effective technique to fabricate various kinds of nanocarbons. This method does not require costly components in its set-up. Thanks to this feature, the initial cost of this method is extremely low compared with any other well-known conventional methods, such as vacuum arc [6], laser ablation [7] and plasma enhanced chemical vapor deposition [8]. So far, carbon nano-onions, multi-wall carbon nanotubes (MWNTs), single-wall carbon nanotubes (SWNTs), single-wall carbon nanohorns (SWNHs), and their metal-included forms, have been successfully synthesized by the ‘arc in liquid’ method using water and liquid nitrogen to host arc discharge [1–5]. Among these reports, the single-walled structures such as SWNTs and SWNHs have been produced only when liquid nitrogen was used in the simple ‘arc in liquid’ method [3]. Under such situation, it was discovered that SWNHs can be produced in water if inert gas is supplied into the arcing