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Production of Y-Junction Carbon Nanotubes by Floating Catalyst Method with a Low Cost and Highly Y- Branched Approach

Same Yousefie[1*], Ali Akbar Mottahedi[2]

[1]Member of Young Researchers club of central Tehran Azad University,
P.O.Box: 14515/775, Tehran, Iran.
[2]Department of Advanced Materials and Renewal Energies
Iranian Research Organization for Science and Technology (IROST)
Forsat St. 71, Ferdoosi Sq., P. O. Box: 15815-3538, Tehran, Iran
Email: mottahedi@irost.org, Tel/Fax: +98(21)88826692
[*]Corres.author: same-yousefie@yahoo.com

Abstract: Growth mechanism of Y-junction carbon nanotubes (CNTs) prepared by floating catalyst method that is base on low-cost approach and highly branched, were synthesized, has been investigated by transmission electron microscopy (TEM). The branch of Y-junction CNT is much shorter than the stem CNT, and the trace of metal particle is observed clearly along the branch carbon nanotube. We present several evidences for a metal particle catalytic growth mechanism and Structural models and Conductance of the branches and also a simple growth model was built to describe the growth process of Y-junction carbon nanotubes.

Key words: Carbon Nanotubes, Y-Junction Growth, Floating Catalyst Method, Chemical Vapor Deposition, Transmission Electron Microscopy.

1. Introduction

Discovery of carbon nanotubes in 1991 by Iijima[1] opened up a new field of research, owing to their unique mechanical, optical and electronic properties, which have shown to be largely dependent on the geometrical chirality's and diameter of the tube[2]. It is hoped that altering these properties may give lead to significant breakthroughs in, for example,

the electronic engineering of materials. These structures are of particular interest to the semiconductor industry, where several nanotube based devices have already been reported[3,4] . The development of electronic devices based on carbon nanotubes allows the possibility of creating junctions that can serve as interconnecting molecular wires[5,6,7] .

1.1. Structure of Y-Junction Carbon Nanotubes

The first structural models for symmetric carbon nanotube Y-junctions based on theoretical calculations[8,9] were proposed shortly after the discovery of multiwall carbon nanotubes by Iijima [1]. Both models are based on the insertion of non-hexagonal (n-H) rings (at least six heptagons) in the hexagonal network in the region where the three branches of the Y are joined together. All the subsequent structural models[10-15] follow the same construction principle of conserving the sp^2 hybridization of the carbon network, differing only in the kind, number and placement of the n-H rings. These variations make possible the constructions of various symmetric and asymmetric model junctions[14] and various angles from Y to T shapes[10] .A Y junction is named symmetric if the three carbon nanotubes joining each other in the Y have identical chirality and the distribution of the n-H rings around the Y is symmetric. Such a junction will be constituted from identical branches oriented at 120°, like in Fig.1a. Whenever one of the above conditions is not fulfilled the junction will be asymmetric, a possible example is shown in Fig.1b.

Figures

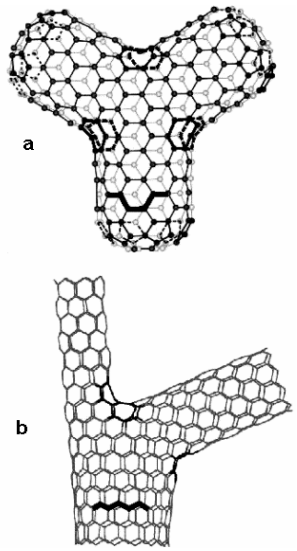

Fig. 1: **Structural models of carbon nanotube Y-junctions. (a) Symmetric, armchair Y junction as proposed by Scuseria [15], the six heptagons are**

For all industrial application of nanotubes, whether single-walled, multiwalled or Y-junctions or other types of nanotubes, efficient and well-controlled synthesis methods are of great importance. In this paper we want to introduce a new optimum method to product Y-junction carbon nanotubes.

1.2. Conductance

Nonconducting bias windows may appear in the Y junction region, even for symmetric junctions built of metallic carbon nanotubes due to the number of the n-H rings and due to the way in which they are arranged[11] .Treboux and co-workers have calculated the properties of a series of spacer elements in the junction regions, which they call 'triangulates', Fig.2. According to their model the complete Y junction is treated as being composed of three semi-infinite, metallic (12, 0) zig-zag carbon nanotubes joined by the triangulate units and the necessary n-H rings to conserve the sp^2 connectivity of the carbon lattice. According to their calculations if the triangulate spacer has an atom centered on the C_3 symmetry axis, Fig.2a. It exhibits no conduction gap, only an electron hole asymmetry, but when the triangulate spacer has a ring centered on the C_3 axis, Fig.2b, a characteristic gap is found in the conductance [20] .

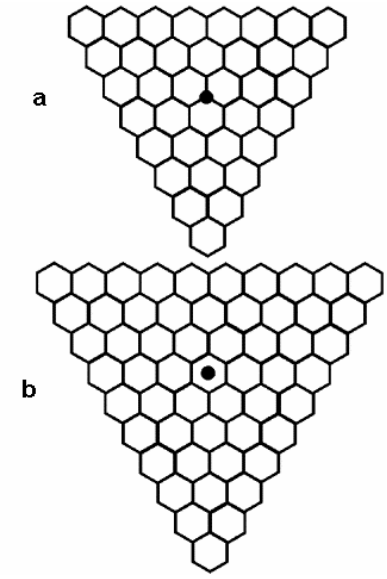

Fig.2: Triangulate spacers as proposed in [11] to join three metallic zig-zag carbon nanotubes into a Y- junction. (a) Triangulate with atom centered C_3 axis; (b) ring centered C_3 axis.

2. Experimental

Fig.3, show a schematic diagram of the experimental setup employed during the course of the present work. A commercial injector is connected to a flask containing the solution of the *N*-hexane as used as the hydrocarbon liquid, and a small amount of thiophene (sulfur additive) is employed. A ceramic tube used as a reactor and installed in a horizontal electric furnace. A hydrocarbon solution with a given composition of ferrocene is introduced into the reactor at a rate of 1.0 ml/min after heating the reactor up to a certain pyrolysis temperature (1150 °C). Hydrogen flows as the carrier gas at a rate of 150 ml/min. The injector is driven by a mixture of hydrogen and has a recirculation system leading the excess liquid away from the injector and back to the flask. The outlet of the injector is fitted to the entrance of a ceramic tube (7 cm in diameter, 120-cm long), which is placed in a horizontal high-temperature furnace. The generated aerosols flow into the heated. When thiophene addition reach an optimal amount (0.38 ml of thiophene and 1.0 g of ferrocene per 100 ml of hexane solution) [24] ,carbon nanotubes with branching structures are obtained in the products. The product and exhaust gas are extracted out from the bottom of the ceramic tube. An additional gas inlet is mounted between the injector and the entrance of the ceramic tube, through which a controlled mixture of hydrogen and carbon gas enters the oven.

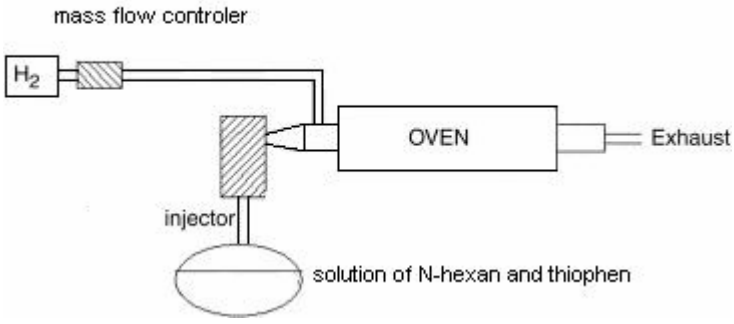

Fig.3: **a schematic diagram of the experimental set-up.**

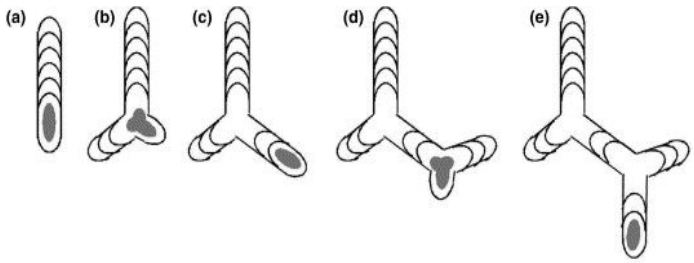

Fig.4: **a schematic diagram of the suggested growth sequence. (a) The growth of a normal nanotube is initiated. (b) The catalyst particle stops and the growth of a branch is initiated (end-growth), the angle between the backbone and the branch is on 120°. (c) The catalyst particle continues moving while growing the back-bone 'tip-growth'. (d, e) The sequence (b, c) is repeated until the growth of the whole tube is terminated.**

3. Results and discussion

The authors attribute the formation of the Y junctions to the catalytic effect of the thiophene present in the gas mixture. The very dramatic changes sulfur may induce in the growth of carbon nanostructures when transition metal catalysts are used has been pointed out by several researchers[16,17] many years ago. More recently, the role of sulfur seems to be very important in the growth of doublewall carbon nanotubes (DWCNTs) [18,19] ,in the absence of sulfur only SWCNTs are produced, while minute amounts of S yield DWCNTs. Sulfur can easily combine with carbon in the gas phase to form S-rich clusters and sulfur may enhance the catalytic activity of transition metals, and it may enhance the metal filling of carbon nanotubes too[20] .The effect of different amounts of thiophene on the morphology of the products has been investigated previously[22,23] ,and it is seen to have a similar effect on the growth of Y-junction carbon nanotubes too.

3.1. Mechanism of Growth

Fig.4 shows a sketch of the proposed mechanism[25] .It is not yet fully understood which parameters induce the growth of branched nanotubes. The unique structures of the Y-junction tubes must be a consequence of the structure and reactivity of the catalyst. It has been demonstrated[18,19] that these two phenomena are responsible for the distinction between the growth of either carbon fibres or nanotubes: A diamond-shaped catalyst

particle favours the growth of carbon fibres with a fishbone-like structure; whereas a near spherical catalyst induces the growth of carbon nanotubes. The rate of diffusion of carbon through the catalyst particle has been shown to determine the orientation of the graphitic layers and the growth direction with respect to the catalyst particle. As such, a higher reactivity of the catalyst particle causes the growth of nanotubes to be more favorable than the growth of fibers.

3.2. Dynamical Simulation

One may observe in Fig.5 that even when the STM tip is not placed right over the center of the junction region due to the spreading of the wave packet tunneling into one of the branches of the Y junction, the STS measurement will 'sample' the junction region, too. This may be the mechanism by which the localized states caused by the n-H rings affect the STS measurements in Ref. [20]

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3.3. Images of Y-junction Carbon Nanotubes:

Through TEM observation, we can see that each Y-junction carbon nanotube has a main CNT stem (Fig 6a and 6b) and a CNT branch which is clearly seen to be extended to form a Y-junction. The CNT branch is much shorter than the CNT stem. The TEM images of Y-junction carbon nanotubes show that the degree of crystallinity of the junction part is very poor with blurry stacking of graphene sheets. The branching angle values are inconstant; some angles are quite sharp; some are obtuse angles or right angles.

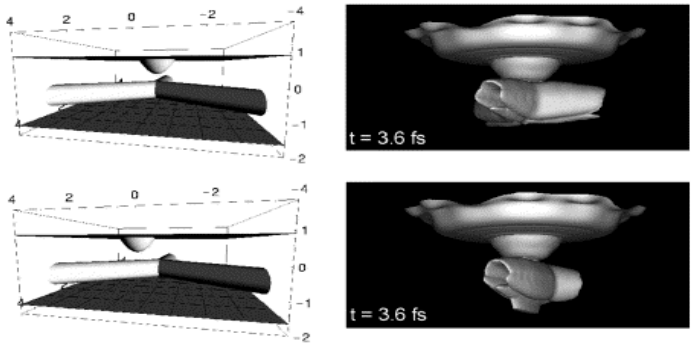

Fig.5: **Wave packet dynamical simulation of geometric effects during the tunneling through a carbon nanotube Y junction placed between the STM tip and a conductive support [21]. Right column: arrangement of the STM tip, Y junction and support. Left column: snapshots of the tunneling process at 3.6 fs. Note that even when the STM tip is placed off-junction a significant amount of charge flows in the junctions region, thus 'sampling' the localized states existing there due to the n-H rings.**

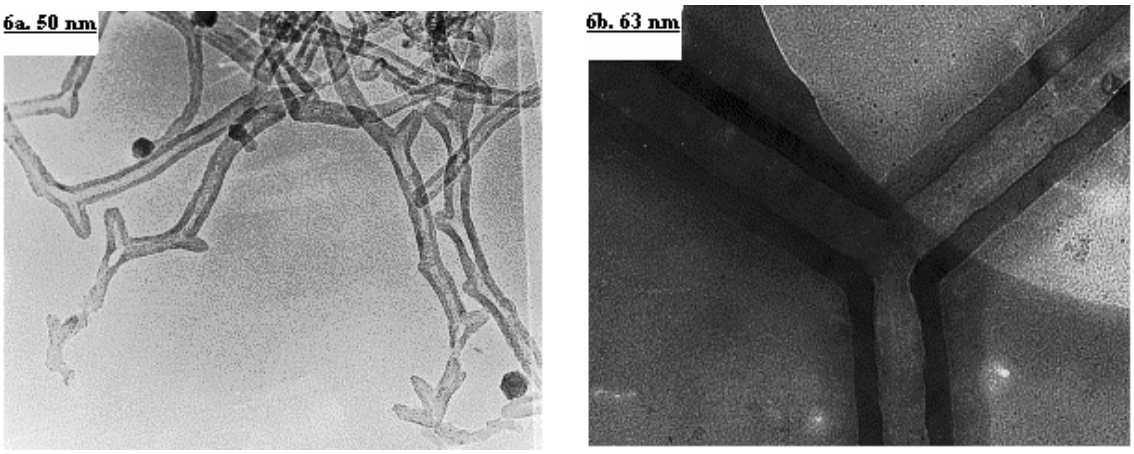

Fig.6a and 6b: **Images of Y-junction carbon nanotubes synthesized, has been investigated by transmission electron microscopy (TEM).**

4. Conclusion

In accordance with early theoretical predictions, in the last years, stable carbon nanotube Y junctions have been produced by various methods. In this paper Y-junction carbon nanotubes are prepared by floating catalyst method. The growth mechanisms of the special structure are analyzed by TEM observation. In these experiments, the Y-junction carbon nanotube has a long stem and a short branch determined by the special metal catalyst growth mechanism under the floating catalytic condition. This is a demonstration that it is possible to synthesis this specific type of nanotube in high purity and at very low cost. And also a better understanding and increased reproductibility for the growth methods has to be achieved and very clearly, once the Y junctions are available on a regular basis many more efforts are needed to understand their electronic, conductivity and etc. properties. So it seems that to be worthwhile to undertake to these challenging tasks due to very exciting application possibilities of Y junctions in nanoelectronics and in composites.

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