Catalytic Chemical Vapor Deposition Preparation of Multi-wall Carbon Nanotubes with Cone-like Heads

Ali Eftekhari,* Sahebali Manafi, and Fathollah Moztarzadeh
Laboratory of Electrochemistry, Materials and Energy Research Center, P. O. Box 14155-4777, Tehran, Iran

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Carbon nanotubes were prepared by catalytic chemical vapor deposition using washable catalyst support of barium and calcium chlorides. It was found that under this experimental condition, carbon nanotubes with cone-like heads are formed. This special shape guarantees easier diffusion and transfer inside the carbon nanotubes due to larger orifices.

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991,[1] there is considerable attention to study different preparative routes to control the CNT structure. In this issue, some special features are needed for specified applications of CNTs. For instance, usually it is needed to prepare open-ended CNTs to use internal structure of the nanotubes. The most common approach is to ball mill the CNTs to break the closed heads of them, but this shortens the nanotubes length.[2,3] On the other hand, it may result in the transformation of CNTs to nanoparticles of amorphous carbon.[4] Thus, it is necessary to find appropriate approach for preparation of open-ended nanotubes.

Here, we communicate some interesting results for simple preparation of CNTs with a desirable orifice structure. To this aim, the most common method viz. catalytic chemical vapor deposition (CCVD) was employed. More recently, we have suggested that using washable catalyst support is accompanied by valuable advantages.[5] In a typical experiment, a catalyst support was prepared from a mixture of barium chloride and calcium chloride in ratio 1:1. Equal amount of citric acid was also added as foaming agent. The amount of Co catalyst, which was obtained from the source of cobalt nitrate, was 1/10 of the catalyst support. All the reagents were dissolved in water and the solution was slowly dried, and the resultant was carefully ground to obtain a fine powder. The catalyst was composed of particles with diameter ranging from 100–300 nm, and was uniformly distributed within the catalyst support as confirmed by EDAX analysis. The resultant catalyst was spread on an alumina boat placed in a horizontal tube furnace. The temperature was raised up to 700 °C under a flow of nitrogen and hydrogen in ratio 10:1. Then, acetylene was injected at a rate of 60 mL/min for 30 min. Purification of the CNTs is very simple, as the catalyst support can be washed easily by water. Small amount of the catalyst can also be removed by a delicate washing process with nitric acid. CNTs were characterized using a Philips XL30 scanning electron microscope and a Philips CM200 transmission electron microscope.

Figure 1 shows SEM image of the CNTs grown on catalyst particles formed on Ba/Ca support using CCVD of acetylene for 30 min at 700 °C. It can be seen that the prepared CNTs are spaghetti-like, long, and curved. The length of vertically aligned CNTs is between 5–10 μm. The acetylene gas first decomposes on the surface of the catalyst particle, then the carbon dissolves in the catalyst, diffuses through it under an activity gradient, and finally the carbon precipitates out on the opposite side of the catalytic particle to form the nanotubes. The diameters of the grown CNTs in Figure 2 are the same as those of cobalt nanoparticles and are between 50 and 150 nm. These are just typical shapes of CNTs. To reveal internal structure of this class of nanomaterials, TEM is an essential technique. In addition to the empty channel of a nanotube, TEM studies indicated a special structure. As can be seen in Figure 2a, this is not simple multiwalled CNTs, as the wall thickness is not constant across the nanotubes as regularly varies in the nanotube heads. In other words, the walls are thinner at the nanotube heads. It seems that the nanotubes head can be considered as a single-wall nanotubes; whereas, the wall can be as thick as tens of nanometer in the middle of the nanotubes (Figure 2b). Since the CNTs are quite long, cone-like structure is only observable on their heads. In a rough estimation from the TEM images, 90% of the CNTs have cone-like heads. The most obvious feature of this structure is easier diffusion through the nanotubes body, as entrance of diffusing species is easy. This is indeed an essential property for most of CNT applications. It has been discussed that diffusing ions need appropriate channels in the size of nanometer for effective diffusion processes.[6,7] Such large orifice of cone-like nanotubes even provides an opportunity for entrance of solid particles as such partial carbon nanoparticles formed during the preparation process (Figure 2c). This is of particular importance, as it is sometimes required to fill CNTs with other active materials. This confirms easier diffusion through such wide orifice. On the other hand, the diameter of the nanotube head can be increased to obtain a trumpet-like shape (Figure 2d).

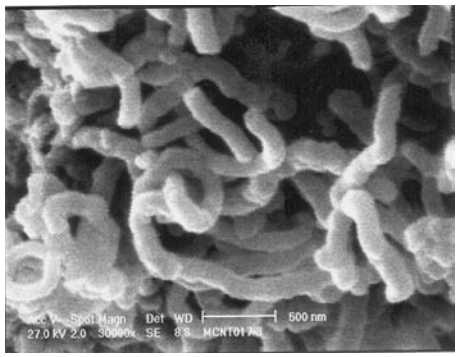

Figure 1. SEM image of the carbon nanotubes grown by means of CCVD using $BaCl_2/CaCl_2$ catalyst support.

It is necessary to evaluate the efficiency of the CCVD process. TG analysis of the sample washed with water (catalyst support was removed, but the catalyst is still included) showed burn of the carbon material at 500 °C, which suggests that the ratio of the carbon prepared to the catalyst is approximately 20:1, which indicates an efficiency of about 95%. Then, it is

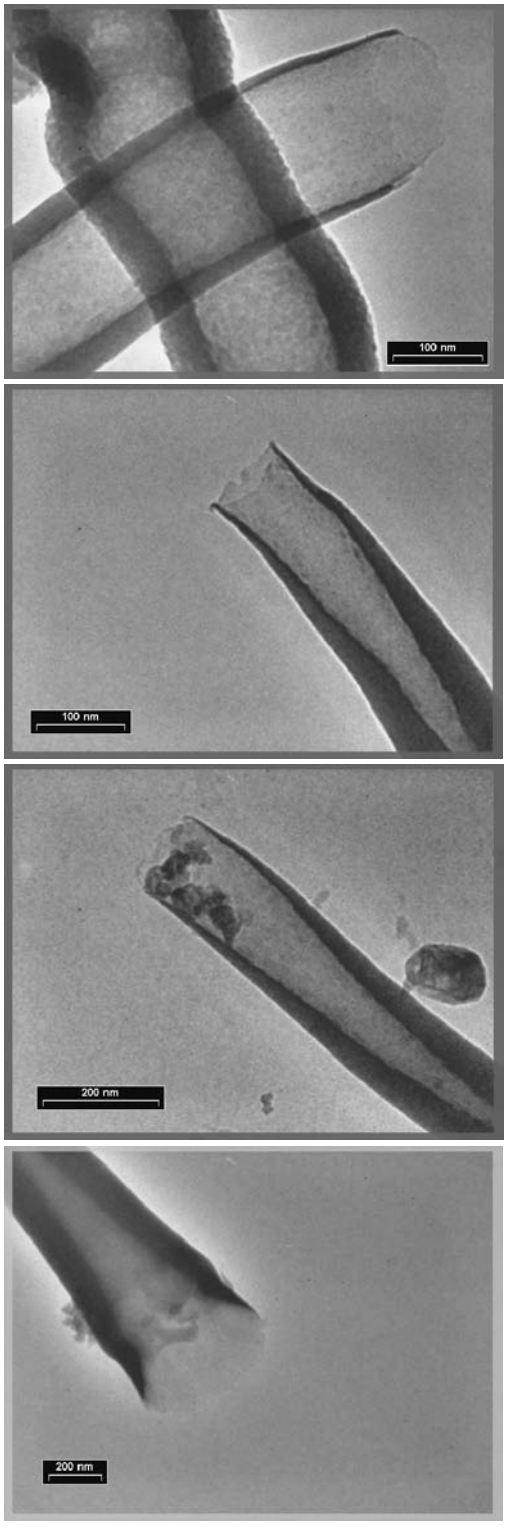

Figure 2. TEM images of individual carbon nanotubes.

needed to distinguish the amount of carbon nanotubes in the carbon material prepared. Raman spectrum of the sample prepared was also investigated. In the high frequency region the ratio between the intensity of the D band (at 1340 cm^{-1}) and the G band (close to 1586 cm^{-1}), noted $I_{D/G}$, is compared. $I_{D/G}$ for these CNTs is about 60%. The G band indicates original

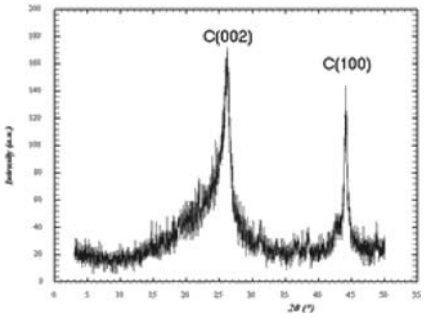

Figure 3. XRD Pattern of the cone-like carbon nanotubes.

graphite features but the D band has been explained as disorder features of graphitic sheets.[8,9] This indicates the ratio of ordered graphite formed during this preparation.

The most important feature of this specific structure is related to the formation of wedge-like walls generating cone-like structure. It is difficult to distinguish individual walls and graphite sheets in TEM images (Figure 2) and even HRTEM images. XRD investigation (Figure 3) provided a possible model for the structure of such wedge-like walls. According to the XRD pattern of the sample, it is obvious that the peak of (100) is as strong as common peak of graphite in carbon nanotubes, i.e. (002). This indicates that the nanotubes walls are not constructed from graphite sheets. This is not the ideal hexagonal graphite as it is also oriented in *c*-axis parallel to the diamond anvil cell axis, and suggests polytype modifications of graphite in the wedge-like walls. Formation of graphite (100) as well as graphite (002) has also been reported in the literature.[10] In this case, the plane of (100) makes an angle with the common graphite of (002), and thus, the graphite sheets are no longer distinguishable. This hypothesis provides a strong reason for the formation such wedge-like walls making the cone-like carbon nanotubes, however, the mechanism of such structure under specified CCVD condition is still unclear which is under investigation.

This simple approach can be used for high-yield and low-impurity preparation of CNTs with desirable structure of cone-like shape. This letter reports the possibility of such simple preparation of this useful nanotubes structure and further investigation can reveal the accurate mechanism of growth and would define a new horizon paths for controlling the structure by experimental condition.

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