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Smallest Freestanding Single-Walled Carbon Nanotube

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ABSTRACT

Here, we report the successful direct observation of the smallest free-standing single-walled carbon nanotube, which has a diameter of about 0.43 nm. Our single-walled carbon nanotubes were produced by the improved floating reactant method, which combines the conventional substrate and floating catalyst methods using zeolite particles as a floating catalyst support. This finding is also important because small-diameter nanotubes were proved to be able to grow without any confinement that limits the tube diameter such as in the tube growth in a template or in the central core of a multiwalled nanotube, as reported in previous studies by other groups. The success of obtaining very small single-walled carbon nanotubes opens the door to unprecedented applications of this fascinating material as a true 1D material.

The quest for small-diameter carbon nanotubes is important for making use of the size effect that is predicted to lead to different properties from those for larger nanotubes.[1] The SWCNTs reported in the present study were produced by a nanozeolite floating-reactant method. The floating-reactant method, primarily used to produce vapor-grown carbon fibers, nanofibers, and nanotubes[2,3] on the basis of the use of small catalytic particles, is one of the most promising methods for the mass production of carbon nanotubes, and it has already been industrialized by several companies worldwide. The zeolite template method[4] is known for its ability to produce thin nanotubes and SWCNTs as well, but it is hard to produce carbon nanotubes in mass. Another method using porous materials such as zeolites is the method of catalytic decomposition of hydrocarbons over supported catalyst[5−7], which allows for easier control of tube quality and production.[8] However, to produce small-diameter nanotubes in a commercial base, a continuous process is favorable. By combining improved versions of both the floating reactant method and the catalyst support method, we obtain a very attractive method for the mass production of thin SWCNTs. We note here that the zeolite used in the present method is not used as a template for the formation of the SWCNT but rather is used to limit the size and structure of the catalytic particles, which have much to do with controlling the diameter and the growth process of the resulting carbon nanotubes. In the present report, we have used a fine zeolite powder as a catalyst support and as a floating substrate and iron as a catalyst to grow small-diameter carbon nanotubes.

Papers have been published on the synthesis and observation of small-diameter nanotubes[9−11] Some concerned the innermost cylinder of a multiwalled tube,[9,11] and another[10] left a margin for argument[12,13] because of specimen preparation or the production method of the tube. Our observation differs from those reported previously in that our observed small-diameter single-walled carbon nanotube (SWCNT) is not on an amorphous film that disturbs the observation nor is it located in the central core part of a multiwalled carbon nanotube that is virtually useless. Another important point is that the small-diameter SWCNTs in the present study were produced in an unconfined system unlike those in previously reported papers, which used a template[10] or the central part of a multiwalled nanotube.[9,11] These distinctions are very important for the advancement of the SWCNT synthesis field and of the related fields of properties measurements and applications to obtain direct visual proof of the existence of the isolated small-diameter SWCNT as reported here.

The material thus obtained was treated with hydrofluoric acid to remove the zeolite and then was washed with nitric acid and observed in the transmission electron microscope (TEM). The TEM used in the present study was a JEOL

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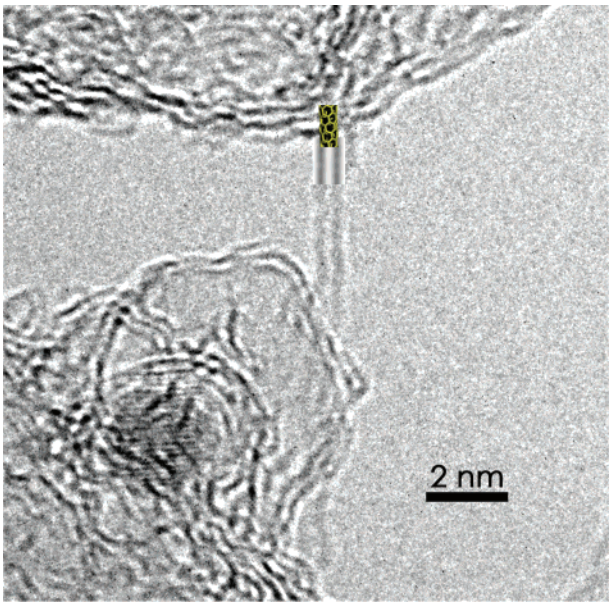

Figure 1. High-resolution transmission electron microscope image of a small SWNT. Inserted images are the model of a (5,1) tube and the TEM simulated image, which is in good agreement with the observation.

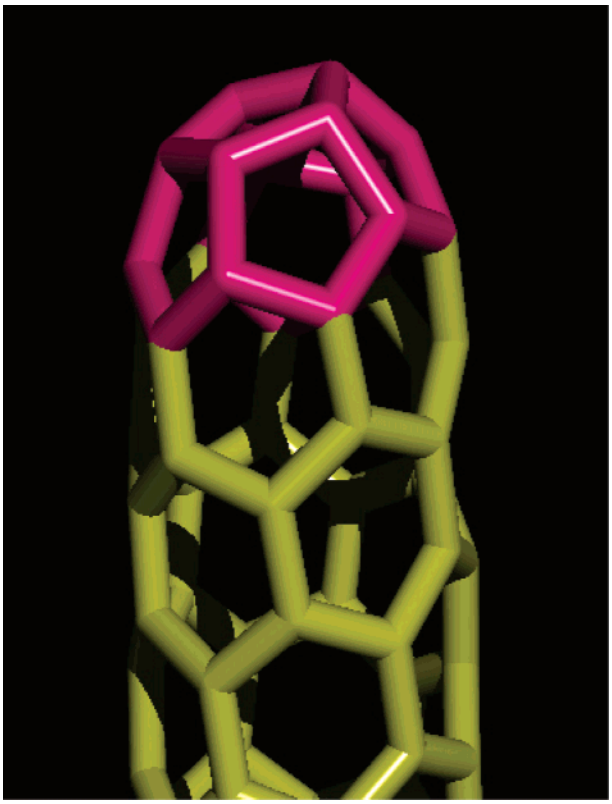

Figure 2. Simulated model of the cap of a (5, 1) nanotube. The cap consists of six pentagonal rings, just like part of a C_{20} molecule, but is slightly deformed.

JEM-2010FEF instrument equipped with an in-column Ω-type energy filter, which greatly contributed to the ease of observation. The operating voltage of the TEM was 200 kV

Low-magnification observations showed that the sample consisted mainly of two parts: bundles of SWCNTs and

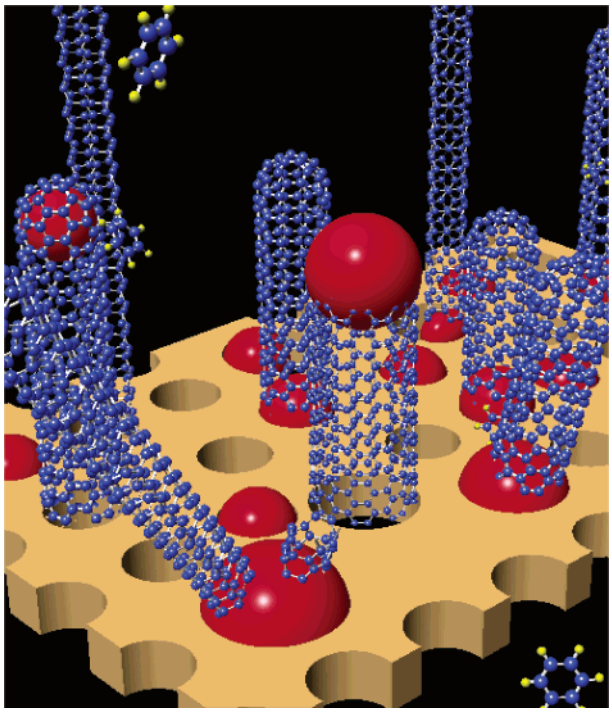

Figure 3. Schematic image of the tip-growth and root-growth models in which the catalytic particles (red balls) are located at the tip and at the root, respectively. The blue balls are the carbon atoms, and the brown base is the simplified model of a zeolite.

large hollow spherical carbon particles. We could also find some metal particles that remained unwashed. Higher-magnification observations showed that the tubes in the bundles were all single-walled nanotubes with a diameter around 1 nm, and the particles were made of rather turbostratic carbon layers. The small-diameter SWCNT, as shown in Figure 1, was found to be isolated from other bundles and could be clearly observed through the use of the energy filter equipped in the TEM. The diameter of the tube was measured to be 0.426 nm,[14] which is the smallest-diameter nanotube yet to be produced by the CVD method, and to our knowledge, it is the smallest-diameter tube ever to be observed as a free-standing or isolated structure. The tube was unstable under electron beam irradiation during TEM observations in comparison with other thicker SWCNTs and deformed within a minute, even when we were trying to bring the camera into focus, showing behavior very similar to that of a polymer sample. From the observed diameter, taking the pixel error due to the digital data acquisition with the CCD camera into account and by comparing with the observed and simulated TEM images of the SWCNT model as shown in the inset of Figure 1, we propose that the nanotube can be assigned the (5, 1) or (4, 2) indices, which give a diameter of 0.436 or 0.414 nm, respectively. We have to stress that it is hard to be sure about the assignment because of the deformation due to the irradiation effect.

We could not find the end of the tube because of the sufficiently long length of the tube and because it is mostly overlapped with either bundles of SWCNTs or with carbon particles. But it is worthwhile to note that the diameter of the small tube is consistent with the diameter of a C_{20}

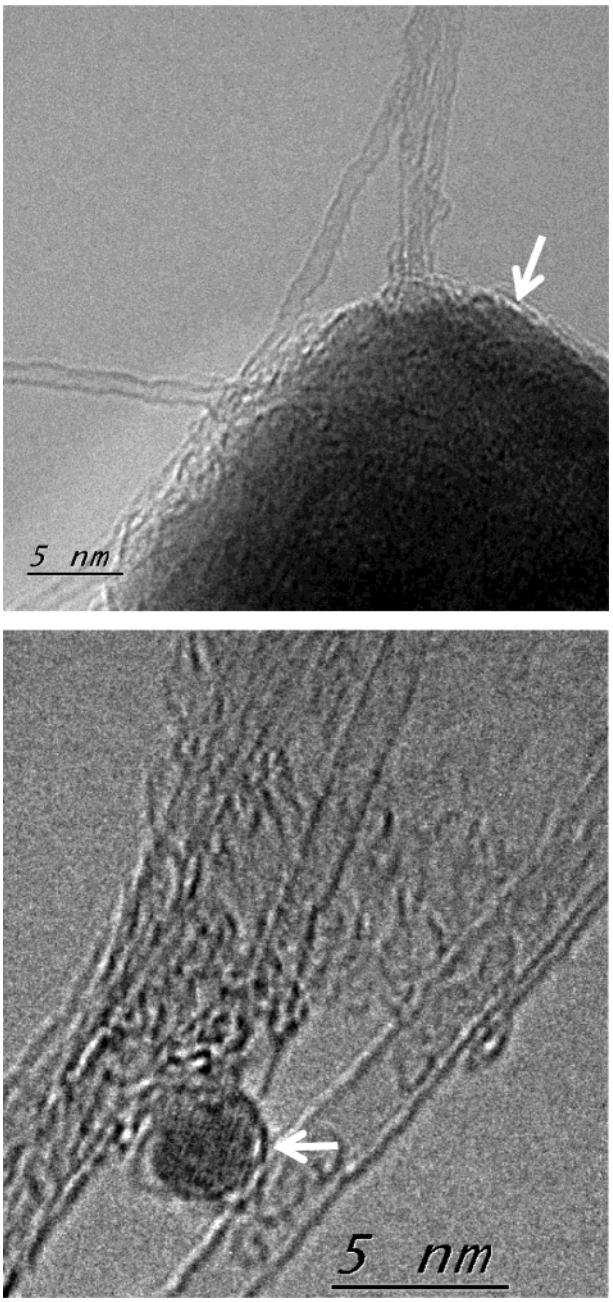

Figure 4. TEM image of the tubes with the catalytic particle (dark contrast indicated by the arrows) at the root of the tubes (top) and at the tip of a tube (bottom). This shows that tube growth in the nanozeolite floating-substrate method occurs both at the root and at the tip of the tube.

molecule,[15] and we can imagine that if there exists an end of a (5, 1) tube then it should be like the model shown in Figure 2, which is capped with six adjacent pentagonal rings and can be closed with no difficulty.

There are two major mechanisms for the catalytic growth of carbon nanotubes depending on the position of the catalyst, where the tube growth occurs. As shown in Figure 3, one is the tip-growth mechanism whereby the catalyst particle is at the tip of the tube, and the other is the root-growth mechanism whereby the catalytic particle is placed at the root of the tube. For the SWCNTs in the present study, as shown in Figure 4, catalytic particles can be found both at the root and at the tip of the tubes. This indicates that two major growth mechanisms coexist in the growth of our small-diameter SWCNT. Moreover, we can imagine that both growth mechanisms are qualitatively the same depending on the position of the catalyst particle that plays a role as a carbon feeding source.

We have shown the successful observation of the smallest free-standing SWCNT and present a production method that is promising for the mass production of small SWCNTs. Such small-diameter SWCNTs, which are virtually equivalent to 1D material, have a wide variety of potential applications such as gas storage devices, energy storage devices, and sensor applications.

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