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Electron microscopic imaging and contrast of smallest carbon nanotubes

Lu-Chang Qin [a,*], Xinluo Zhao [b], Kaori Hirahara [b], Yoshinori Ando [c], Sumio Iijima [a,b,c,d]

[a] *JST-ICORP Nanotubulite Project, c/o NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan*
[b] *JST-ICORP Nanotubulite Project, c/o Meijo University, Tenpaku-ku, Nagoya 468-8502, Japan*
[c] *Department of Materials Science and Engineering, Meijo University, Nagoya 468-8502, Japan*
[d] *R&D Group, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan*

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Abstract

The weak scattering from smaller carbon nanotubes results in weak contrast in their electron microscope images, and observation and interpretation of such images require special attention in order to avoid erroneous conclusions. It is demonstrated that the 4 Å carbon nanotube, residing inside a multi-walled carbon nanotube, bears recognizable signature in its image contrast for identification. For an isolated single-walled carbon nanotube, observation should be made in areas where the nanotube is exposed. When the carbon nanotube is overlapped with a supporting glassy carbon film, it is practically impossible for the nanotube to produce usable contrast features for unambiguous identification. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Many of the extraordinary properties of carbon nanotubes are strongly linked to their diameter which is on the nanometer scale. 7 Å, the diameter of C_{60} fullerene [1], which had been considered to be the smallest possible due to a belief that the structure is governed by the isolated pentagon rule, which stipulates that no adjacent pentagons are formed in the cage structure. Carbon nanotubes [2] had been considered to be limited by the same isolated pentagon rule due to a hypothesis that carbon nanotubes were grown out of fullerenes and therefore the smallest carbon nanotube was considered to be of diameter 7 Å [3]. Experimental evidence for carbon nanotubes of this diameter was observed soon after the announcement of the discovery of carbon nanotubes [4]. Energetically, the stability of a carbon nanotube is secured by the compensation of energy saved when the number of dangling bonds was reduced in rolling up a section of graphene at the expense of strain energy owing to the increasing curvature. Therefore, a balance is maintained by these two competing factors, which in turn determine the smallest diameter. Calculations indicate that

* Corresponding author. Fax: +81-298-501366.
E-mail address: qin@frl.cl.nec.co.jp (L.-C. Qin).

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carbon nanotubes are energetically stable down to a diameter as small as 4 Å [5,6].

However, with the discovery of C_{36}, it is demonstrated experimentally that the isolated pentagon rule can be violated while a stable structure is formed [7]. The subsequent successful synthesis of C_{20} [8], which is composed of only pentagons in its topological structure, exemplifies that the isolated pentagon rule can even be disregarded as this structure assumes a structure that is in maximum violation of the isolated pentagon rule. Given the close link between the fullerenes and carbon nanotubes in structure, it is not surprising that carbon nanotubes of diameters corresponding to those of C_{36} and C_{20}, respectively, were reported based on primarily electron microscopy observations [9–12]. Furthermore, using molecular dynamics simulations and electron microscopy, Peng et al. [13] suggested a configuration of even smaller diameter that is stable structurally, though it is unstable energetically.

2. Results and discussion

Carbon nanotubes of 4 Å diameter have been produced with an improved arc-discharge technique in using hydrogen as the carrier gas [14]. No metal catalysts were necessary in the arc-discharge process. When the conditions, under which the arc-discharge was conducted, are well controlled, multi-walled carbon nanotubes with very small inner diameters are produced [10]. Fig. 1 shows an electron microscope image of a multi-walled carbon nanotube produced with the arc-discharge technique where the innermost shell has a diameter of 4 Å. Among the observed nanotubes, the number of walls, as well as the diameter of the innermost shell, varied, but the innermost shells appeared to be much smaller than the nanotubes prepared under usual conditions. Apart from the nanotubes with an innermost shell of 4 Å diameter, slightly thicker ones were also often observed, including those of diameters 5 and 7 Å, corresponding to the diameters of C_{36} and C_{60}, respectively. With the synthesis technique developed for this work, it should be noted that the smallest nanotubes are produced in large numbers.

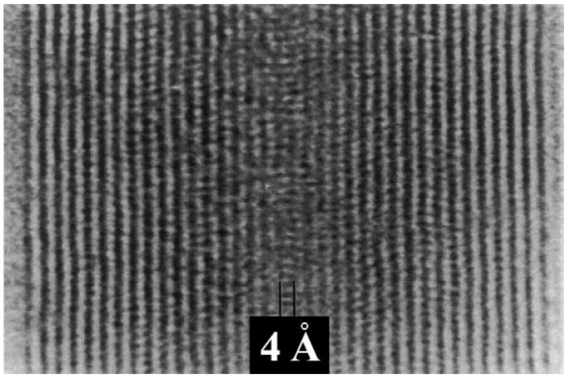

Fig. 1. Electron microscope image of a multi-walled carbon nanotube with the smallest nanotube as its innermost shell. The innermost tubule has a diameter of 4 Å. Each dark line corresponds to a single side wall of the nanotube.

The central question is how to identify the nanotubes of the smallest diameter. Although it can often be used as evidence showing the tubular structure of a nanotube, the hollow core of a multi-walled carbon nanotube is hardly noticeable when the innermost diameter becomes 4 Å, which is very close to the graphite (0 0 2) spacing ($d =$ 3.4Å) that is also usually observed between the neighboring shells of multi-walled carbon nanotubes as seen in Fig. 1. On the other hand, it should be pointed out that a characteristic feature of Fig. 1 is that the image contrast diminishes in a non-linear manner as it moves towards the axis of the nanotube. Remarkable difference can be observed in the image contrast of various shells of different diameters, in particular among the few shells next to the tubule axis. This is because the smaller nanotubes have fewer carbon atoms and therefore possess weaker scattering power. This contrast feature is not observed in graphite where all graphene sheets give rise to equal contrast when aligned properly. To confirm this characteristic contrast behavior quantitatively, Fig. 2 shows the matching and comparison between an experimental image (top portion) and a simulated image (bottom portion). The fading contrast toward the center of a multi-walled carbon nanotube serves as a signature of the tubular nature of the structure and it can be used in practice for identifying tubular structures.

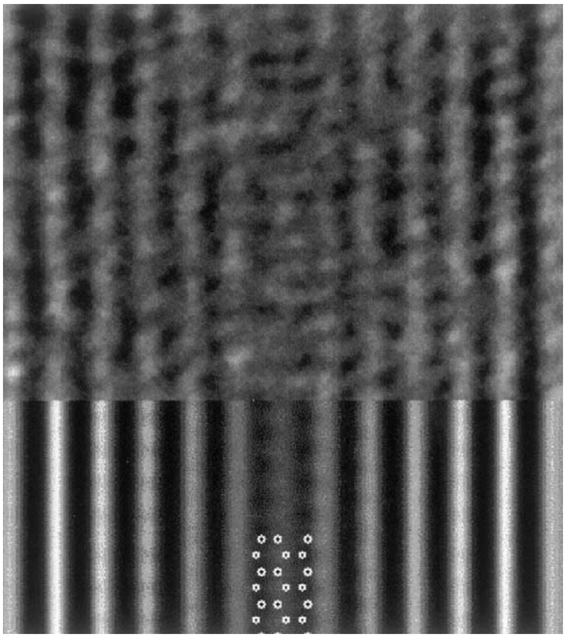

Fig. 2. Comparison of experimental (top) and simulated (bottom) images. The contrast due to the graphene shells fades towards the center. The open circles in the simulated image indicate the atoms belonging to the 4 Å nanotube in projection.

Single-walled carbon nanotubes [15] produce only weak contrast in electron microscope images, and are always much more difficult to be observed comparing with the multi-walled ones. In practice, actual observations should always be made in areas where the nanotubes are suspended without direct support of a film such as a lacey carbon film. Observations are best viewed through the holes specifically made for such purposes. Consequently, great caution must be exercised to assign experimental images to revealing single-walled carbon nanotubes.

In order to establish usable criteria for such observations, we also carried out numerical simulations to examine the contrast behavior of single-walled carbon nanotube images with particular attention being paid to the situation when there is a supporting film overlapping with the nanotube. The model structure used for the simulations is given schematically in Fig. 3A. It consists of two parts: a single-walled carbon nanotube of 4 Å diameter and a supporting glassy carbon film (with a

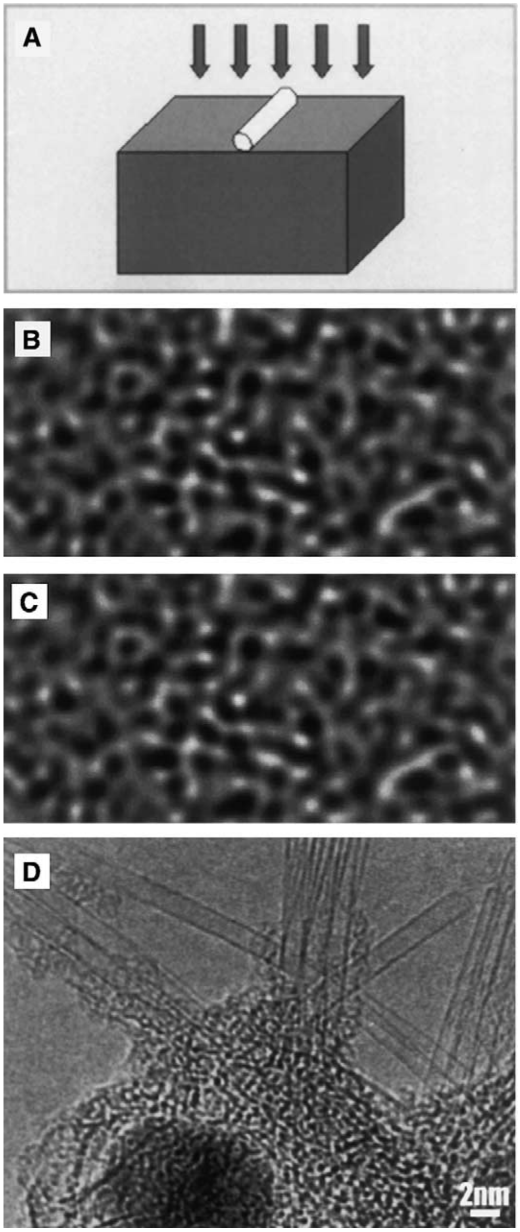

Fig. 3. (A) Model structure where a 4 Å single-walled nanotube is lying on top of a lacey carbon film. The arrows indicate the incident electron beam. (B) Simulated electron microscope image of the composite structure shown in (A) with the film thickness 37 Å. (C) Simulated image of the glassy film without nanotube. The images in (B) and (C) are indistinguishable. (D) Experimental electron microscope image showing that when a single-walled carbon nanotube is in overlap with a glassy carbon film, the image contrast due to the nanotube is overwhelmed by the glassy film.

mass density of 2.0 g/cm^3) of various thicknesses. In Fig. 3B the image is obtained under optimum imaging conditions from a glassy carbon film of thickness 37 Å with a 4 Å single-walled carbon nanotube lying on top of the film. The nanotube on the top of the film gives rise to undetectable contrast and therefore the presence of the nanotube cannot be revealed in such a structure. This point is affirmed further by comparing the electron microscope image with that of the supporting film alone as shown in Fig. 3C. The difference between Figs. 3B and C is indistinguishable. This contrast feature applies to various film thicknesses down to 11 Å. The diminishment of the contrast difference is because of the fact that the glassy carbon film gives rise to much stronger scattering than the few atoms comprising the nanotube of 4 Å diameter. As a matter of fact, when it passes through the structure, the incident electron beam encounters at most only two carbon atoms along its path in the beam direction, while several more atoms are encountered along its path going through the glassy carbon film. When the film gets thicker, it would become even more difficult to distinguish the images with a nanotube from those without. In order to illustrate this further, Fig. 3D shows an experimental electron microscope image, where single-walled carbon nanotubes co-exist with an amorphous carbon film. It is clearly shown that, when the carbon nanotube is overlapped with an amorphous film, the image contrast due to the nanotube becomes indistinguishable.

On the other hand, if the nanotube is aligned almost parallel to the incident electron beam, owing to the higher density of projected potential from the nanotubes onto the supporting film, the traceable contrast from the nanotube could survive through a somewhat thicker film. It will depend on the relative tilting angle of the nanotube with respect to the incident electron beam. Nonetheless, it would hardly survive over a long distance. Basing on these analyses, we argue that the double-line contrast observed in [11] is unlikely to have arisen from the 4 Å single-walled carbon nanotubes as suggested. Instead, it is more likely due to the double-layer graphitic stacks, in which the slightly larger separation of about 4 Å was caused by a relaxation of the inter-layer van der Waals interactions when there are only two layers [16].

When the film becomes thinner, the nanotube contrast would gradually emerge. Fig. 4A shows a simulated electron microscope image of a supporting glassy carbon film of only 7.4 Å thick. When there is a 4 Å nanotube on top of the film, the line contrast due to the nanotube could be recognized as shown in Fig. 4B. For comparison, Fig. 4C shows the same image as in Fig. 4B, but the projected atomic positions of the nanotube are indicated with open circles. As expected, if the film becomes even thinner, the image contrast due to

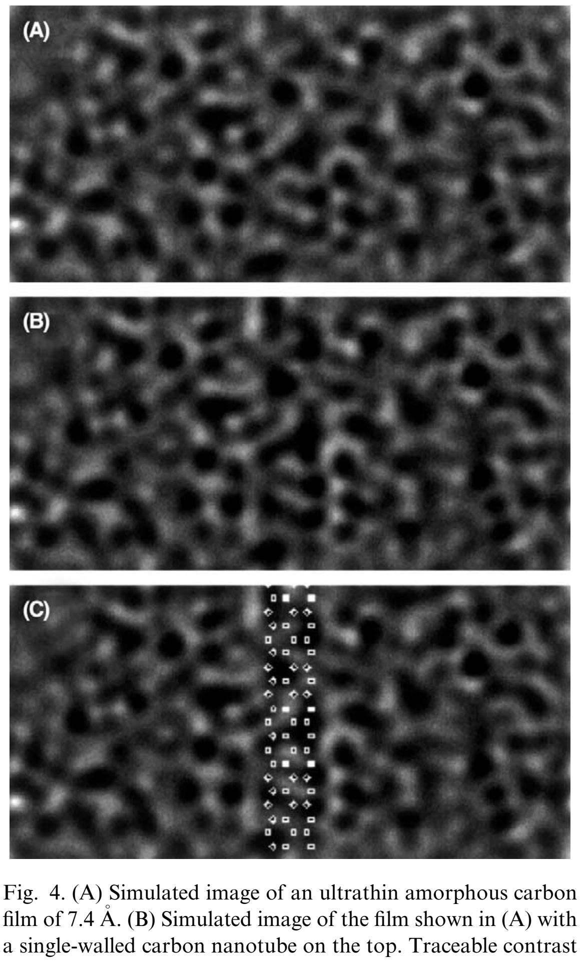

Fig. 4. (A) Simulated image of an ultrathin amorphous carbon film of 7.4 Å. (B) Simulated image of the film shown in (A) with a single-walled carbon nanotube on the top. Traceable contrast due to the nanotube could be identified in comparison with the bare glassy film shown in (A). The projected atomic positions of the 4 Å nanotube are indicated with the open circles in (C).

the nanotube would become more apparent. Detailed calculations show that, in order to observe single-walled carbon nanotubes of 4 Å diameter, one must avoid areas where the nanotube is overlapped with the film, since in practice, it is almost impossible to obtain glassy carbon films of thickness 10 Å or thinner.

In addition to the method of contrast analysis discussed above, the tubular nature of carbon nanotubes can also be verified with rotation experiment as demonstrated by Wang et al. [17]. However, this method requires longer exposure of the nanotube to the incident electron beam and it could be difficult since the single-walled carbon nanotube is very sensitive to the electron beam irradiation.

The multi-walled carbon nanotubes with smallest cores are expected to have much lower values of compressibility than graphite and polygonization observed in single-walled carbon nanotubes is not expected to occur under pressure [18].

3. Conclusions

When the smallest carbon nanotube is formed inside a multi-walled carbon nanotube, the electron microscope image contrast fades towards the center of the image. The contrast characteristic is confirmed with both image simulations and experimental observations. For the case of single-walled carbon nanotubes, experimental observation should be made in areas where there is no overlapping with the commonly used glassy carbon supporting film to avoid erroneous interpretation of the experimental images.

References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature (London) 318 (1985) 162.
[2] S. Iijima, Nature (London) 354 (1991) 56.
[3] M.S. Dresselhaus, G. Dresselhaus, R. Saito, Phys. Rev. B 45 (1992) 6234.
[4] P.M. Ajayan, S. Iijima, Nature (London) 358 (1992) 23.
[5] D.H. Robertson, D.W. Brenner, J.W. Mintmire, Phys. Rev. B 45 (1992) 12592.
[6] S. Sawada, N. Hamada, Solid State Commun. 83 (1992) 917.
[7] C. Piskoti, J. Yarger, A. Zettl, Nature (London) 393 (1998) 771.
[8] H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl, J. Wörth, L.T. Scott, M. Gelmont, D. Olevano, B.V. Issendorff, Nature (London) 407 (2000) 60.
[9] L.F. Sun, S.S. Xie, W. Liu, W.Y. Zhou, Z.Q. Liu, D.S. Tang, G. Wang, L.X. Qian, Nature (London) 403 (2000) 384.
[10] L.-C. Qin, X. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando, S. Iijima, Nature (London) 408 (2000) 50.
[11] N. Wang, Z.K. Tang, G.D. Li, J.S. Chen, Nature (London) 408 (2000) 50.
[12] H.Y. Peng, N. Wang, Y.F. Zheng, Y. Lifshitz, J. Kulik, R.Q. Zhang, C.S. Lee, S.T. Lee, Appl. Phys. Lett. 77 (2000) 2831.
[13] L.-M. Peng, Z.L. Zhang, Z.Q. Xue, Q.D. Wu, Z.N. Gu, D.G. Pettifor, Phys. Rev. Lett. 85 (2000) 3249.
[14] X. Zhao, M. Ohkohchi, M. Wang, S. Iijima, T. Ichihashi, Y. Ando, Carbon 35 (1997) 775.
[15] S. Iijima, T. Ichihashi, Nature (London) 363 (1993) 603.
[16] S. Iijima, Chem. Scripta 14 (1978 and 1979) 117.
[17] N. Wang, K.K. Fung, W. Lu, S. Yang, Chem. Phys. Lett. 229 (1995) 587.
[18] J. Tang, L.-C. Qin, T. Sasaki, M. Yudasaka, A. Matsushita, S. Iijima, Phys. Rev. Lett. 85 (2000) 1887.