DIRECT OBSERVATION OF INTERCALANT AND CATALYST PARTICLE IN SINGLE WALL CARBON NANOTUBES

X. FAN[1,2], E. C. DICKEY[2], P. EKLUND[3*], K. WILLIAMS[3], L. GRIGORIAN[3†], A. PURETZKY[1], D. GEOHEGAN[1], R. BUCZKO[1,4††], S. T. PANTELIDES[1,4] and S. J. PENNYCOOK[1,4]

[1]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831
[2]Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY, 40506
[3]Department of Physics and Astronomy, University of Kentucky, Lexington, KY, 40506
[4]Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235,
* Current address: 104 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802-6300
† Current address: Fundamental Research Lab, Honda R&D Americas, Inc., 100 Town Center, Suite 2050, Southfield, MI 48075
†† Permanent address: Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland

ABSTRACT

The Z-contrast scanning transmission electron microscopy (STEM) imaging technique has been used to study dopant atoms and catalyst particles in single wall carbon nanotubes (SWNT). Iodine and bromine have been doped respectively in arc-grown SWNTs. We have directly observed the dopant sites and distributions. Both dopants appear to be incorporated linearly within the SWNT bundles. SWNT were also grown by pulsed laser ablation with mixed Ni and Co catalyst, and the size and distribution of catalytic particles was studied. By using Z-contrast imaging, we found that the size distribution of the catalyst particles varied over a large range, but even the smallest were larger than the diameter of an individual SWNT. Furthermore, electron energy loss spectroscopy (EELS) is used to determine the composition of individual nano-catalyst particles, and were found to consist of a uniform alloy of Co and Ni.

INTRODUCTION

Since the discovery of carbon nanotubes[1], their remarkable electronic and structural properties have promised to revolutionize application ranging from nanoscale electronics to ultralightweight structural materials [2]. Transmission electron microscopy (TEM) has played a very important role in the discovery and early stage of development. As many other techniques have been developed to study the numerous properties of carbon nanotubes, TEM has become an important technique to check the quality of new samples created by the ever-increasing new growth techniques.

Furthermore, electron microscopy can provide critical insights for the study of carbon nanotubes where no other technique can substitute. Here we show that by using the Z-contrast imaging technique in a scanning transmission electron microscope (STEM), we can distinguish high-Z elements incorporated inside carbon nanotubes with high sensitivity, including dopant atoms/molecules and catalyst particles.

Single wall carbon nanotubes (SWNTs) have been shown to be amphoteric in character, i.e., they can exchange electrons with a dopant atom (or molecule) to form the corresponding positively or negatively charged counter ion [3,4]. Using the SWNT grown by the arc-discharge

Mat. Res. Soc. Symp. Proc. Vol. 593 © 2000 Materials Research Society

method[5], tubes were doped either by bromine in its vapor phase[4], or iodine by immersion in molten iodine[6], as described previously. In both cases, resistivity and Raman scattering studies indicated charge transfer and significant increase of conductivity. Doping of iodine appears to be unique to carbon nanotubes as iodine does not intercalate other carbon polymorphs. Raman scattering showed charged polyiodide chains to be distributed throughout the bundles, and it has been generally assumed that the intercalant enters the interstitial channels between tubes. Little is known, however, about the actual dopant sites and distributions. In this letter, we present Z-contrast STEM images that directly reveal the distribution of iodine atoms and bromine within arc-grown SWNT bundles, respectively.

The SWNT grown by pulsed laser ablation was performed using a similar setup to that used by Guo et al.[7] The graphite target contains 1 at.% each of Ni and Co powders, and further experimental details have been described elsewhere [8]. A high yield of SWNT bundles were obtained containing high densities of catalyst particles. As regards the growth mechanism of carbon nanotubes, it is generally believed that the catalyst size determines the tube diameter. In the case of chemical vapor deposition (CVD) grown multi-wall carbon nanotubes, catalyst particles are found inside the tubes, and often at their tips, and typically range from a few nanometer to tens of nanometers in size. Therefore, as the typical SWNT has a diameter around 1-2 nm or less, it is natural to assume the presence of catalyst particles around 1 nm diameter or less in the SWNT. To understand the growth process therefore it is critical to determine the location of these particles, e.g. whether these particles are at the tip of each individual SWNT. Furthermore, it is also possible the metal catalyst atoms are dispersed within the single carbon layer, which may indicate a completely different growth mechanism. All these questions can be answered with Z-contrast imaging with single atom sensitivity.

EXPERIMENTAL

Nanotube samples were prepared by dipping holey carbon grids in ethanol and then placing them in contact with the dry, as-prepared materials, in powder form. After baking the grid on a heating lamp for about 10 min, the sample was ready for imaging.

Images were taken with a VG Microscopes HB603U STEM, operating at 300 kV. This microscope has demonstrated information transfer in Z-contrast images at the sub-angstrom level [9] and direct imaging of individual heavy atoms on a light support [10]. Of particular relevance to this work is the fact that the Rutherford scattering used to form Z-Contrast images scales with the square of the atomic number [11] resulting in large contrast between C (Z=6) and other elements, e.g. I (Z=53), Br (Z=35).

EELS spectra are collected simultaneously with the Z-contrast image on a VG Microscopes HB501 STEM also fitted with a high-resolution objective lens, capable of forming a probe 0.22 nm diameter. Therefore spectra can be collected from *individual* catalyst nanoparticles.

RESULTS

Dopant distributions

Fig. 1 shows STEM images of iodine doped SWNT bundles, comparing bright field and Z-contrast images from regions in the sample where several individual tubes can be distinguished[12]. Whereas the bright field image shows very little contrast and is ambiguous as to the position or even presence of I, the dark field image directly reveals the projected I distribution. Comparing the two images, it is seen that the iodine is incorporated within one particular nanotube (labeled A) but is not present in others in the bundle (e,g, nanotube B). From

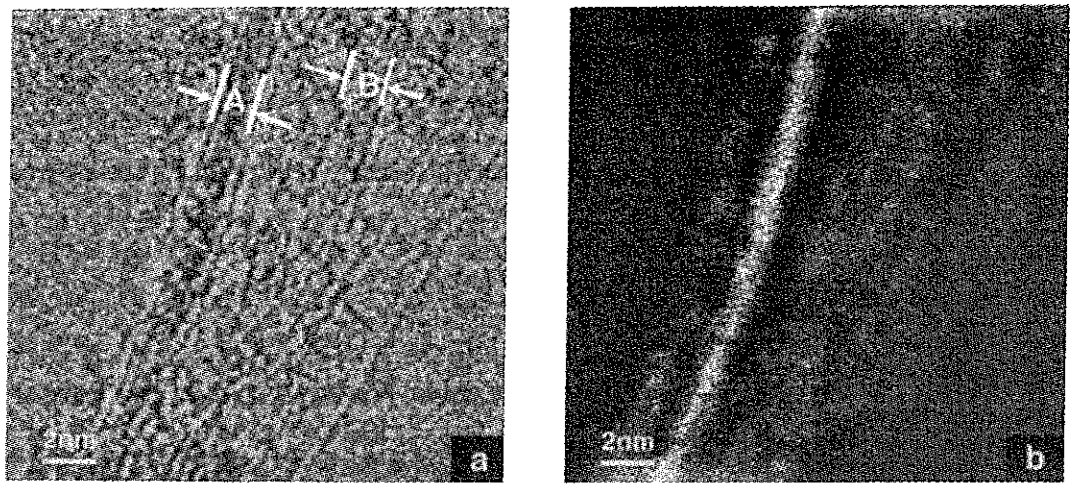

Fig.1 (a) Bright field phase contrast image and (b) dark field Z-contrast images of a SWNT bundle taken simultaneously on the STEM. The conventional phase contrast image is useful for locating the nanotube walls; the precise registry of the two images therefore allows the iodine distribution to be determined to high precision. Iodine is clearly inside some tubes, such as A but not others, for example B.

the width of the bright stripe, ~ 0.65 nm, it is clear that the iodine is incorporated *inside* the tube since the diameter of the tube is 1.36 nm.

Similar results are obtained for Br doped SWNT. As shown in Fig.2, a linear chain of Br atoms is distributed along the axial direction of a SWNT bundle. The current resolution does not resolve the location of the Br chain with respect to the SWNT bundle.

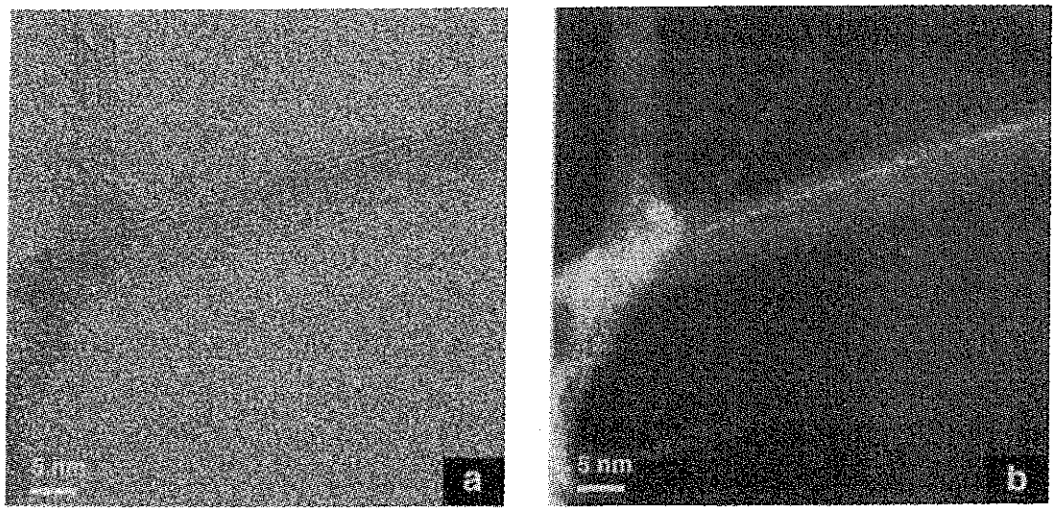

Fig.2 (a) Bright field phase contrast image and (b) dark field Z-contrast images of a bromine doped SWNT bundle, taken simultaneously on the STEM. The bright line in the Z-contrast image indicate that the Br intercalated linearly inside the nanotube bundle but it is unclear whether it is inside an individual nanotube or on an interstitial site.

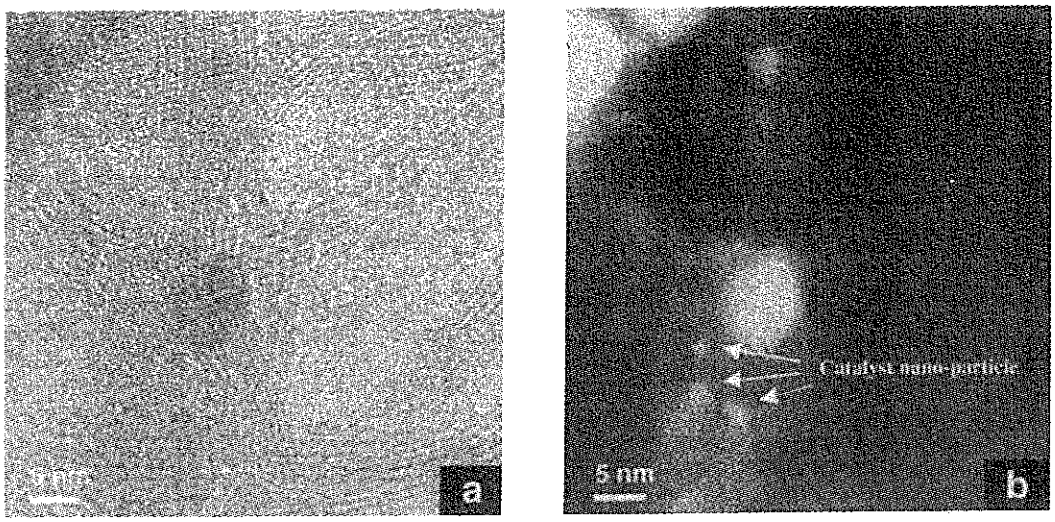

Fig 3 (a) Bright field phase contrast image and (b) Z-contrast dark field image taken simultaneously on a pulsed-laser ablation generated carbon nanotubes. The bright field image clearly shows the bundles of the single wall carbon nanotubes. The Z-contrast image shows distinctively the catalyst nanoparticles especially those of 2-3nm size which barely resolved in the bright field image. No sub-nanometer particles are observed.

Catalyst distributions

Catalyst particles as small as 2-3 nm in diameter were observed using Z-contrast imaging (Fig. 3(a)), which are barely seen in the phase contrast image (Fig. 3(b)). No smaller particles or individual metal atoms were observed within the SWNT bundles, which is also confirmed by electron energy loss spectroscopy in the next section. The size distribution of the catalyst particles extends over a large range from a few nanometers to at least 30 nm (Fig. 4). Contrary to common belief, we find that large size (20nm) catalyst particles can grow SWNT.

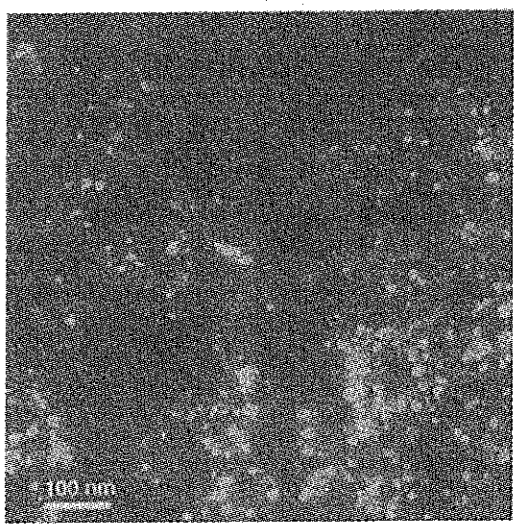

Fig 4 Z-contrast image showing catalyst particles in a web of pulsed laser ablation produced single-wall carbon nanotube bundles. The diameters of the catalyst range from 2-30nm.

The composition of individual catalyst nanoparticle can be determined by EELS. Both Co and Ni are found within each individual particle at an almost constant ratio, as shown in Fig.5. This indicates that Ni and Co have intermixed to form *alloy* clusters.

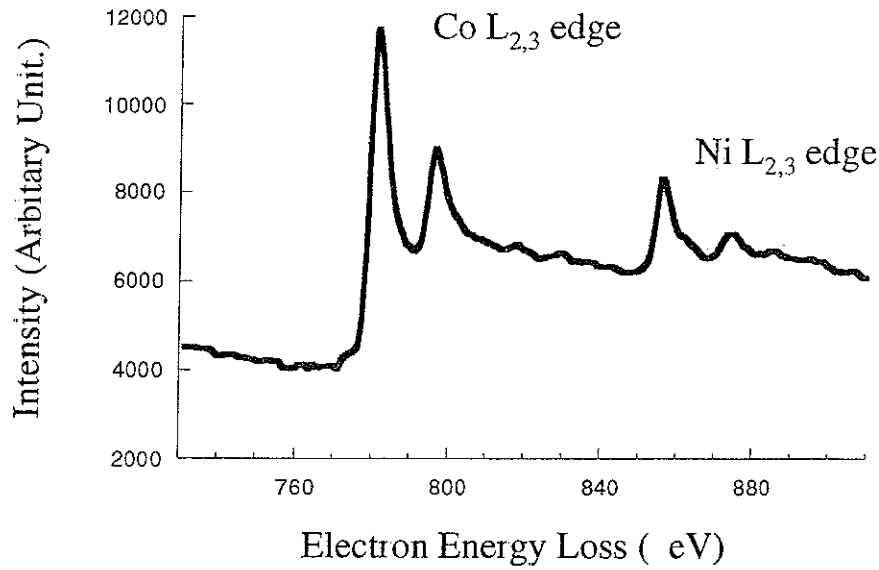

Fig. 5 Electron energy loss spectrum of a single 5 nm size catalyst particle. The presence of both Co and Ni L-edge and their nearly constant ratio in different areas of the particle shows clearly uniform distribution of Co and Ni in each catalyst particle, possibly in the form of alloy

CONCLUSION

In summary, this work provides a new perspective on the study of carbon nanotubes by Z-contrast imaging. It has shown that Z-contrast imaging is an especially powerful method to investigate foreign elements in carbon nanotubes due to differences in atomic number. The high sensitivity of Z-contrast imaging can determine non-crystalline structures at near-atomic level.

The determination that dopant atoms are contained *within* carbon nanotubes not only suggests the doping mechanism, but also provides the experimental basis for future theoretical studies of the effects of intercalated atoms on the electronic structure of carbon nanotube.

ACKNOWLEDGEMENT

This research was sponsored by the NSF-MRSEC Advanced Carbon Materials Center under grant No. DMR-9809686, and by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp and the Laboratory-Directed Research and Development Program at ORNL.

REFERENCES:

1. S. Iijima, Nature, **354**, 56, (1991).
2. B. Yakobson, R.E. Smalley, Amer. Scientist, **85,** 324 (1997).
3. R.S. Lee, H.J. Kim, J.E. Fischer, A. Thess and R. E. Smalley, Nature **388**, 255 (1997).
4. A.M. Rao, P.C. Eklund, S. Bandow, A. Thess, and R.E. Smalley, Nature **388**, 257 (1997).
5. C. Journet, et al., Nature **388**, 756 (1997).
6. L. Grigorian, K. A. Williams, S. Fang, G.U. Sumanasekera, A.L. Loper, E.C. Dickey, S.J. Pennycook, and P.C. Eklund, Phys. Rev. Lett. **80**, 5560 (1998).
7. T. Guo, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Chem. Phys. Lett. **236**, 419 (1995).
8. A.A. Puretzky, D.B. Geohegan, X. Fan and S.J. Pennycook, Appl. Phys. Lett. in press, (1999).
9. P.D. Nellist and S. J. Pennycook, Phys. Rev. Lett. **81**, 4156 (1998).
10. P.D. Nellist and S. J. Pennycook, Science **274**, 413(1996).
11. D.E. Jesson and S.J. Pennycook, Proc. R. Soc. Lond. A **449**, 273 (1995).
12. X.Fan, E. C. Dickey, P. Ecklund, K. Williams, L. Grigorian, R. Buczko, S. T. Pantelides and S. J. Pennycook, Phys. Rev. Lett., submitted. (1999)