HITACHI SCIENTIFIC INSTRUMENT
TECHNICAL DATA TEM

SHEET NO. 114

SUBJECT: HIGH TEMPERATURE AND HIGH RESOLUTION OBSERVATION AND EELS ANALYSIS OF CARBON NANO-TUBES

INSTRUMENT: HF-2200 COLD FIELD EMISSION TRANSMISSION ELECTRON MICROSCOPE AND DIRECT SPECIMEN HEATING SYSTEM
EMAX7000 ENERGY DISPERSIVE X-RAY SPECTROMETER

CONTENTS

1. INTRODUCTION

Carbon nano-tubes have been extensively studied worldwide. They are targeted on electron emitters[1)~3)], and surface acoustic wave (SAW) filters in the field of electronics/information/communications and also on lightweight batteries and hydrogen storage materials in the field of energy. Transmission electron microscopes are one of the indispensable instruments needed for the study of carbon nano-tubes. These tubes, however, are sensitive to high energy electron beam irradiation so that they often change their micro-structures during observation. For high resolution microscopy and analysis of these tubes a high level of technical expertise was needed[4)~5)].

There are two types of carbon nano-tubes; MWNT or multi-walled nano-tube and SWNT or single-walled nano-tube [7)]. MWNT is composed of 2 to 30 layers of graphite sheets. SWNT is a closed seamless tube of mono-atomic layer of graphite or graphene. We reported on high resolution microscopy of MWNT which was stable under 200 kV beam thanks to heating in the TEM specimen chamber. See Technical Data TEM Sheet No. 112. In this Technical Data TEM Sheet No. 114 we report on high resolution microscopy and EELS or Electron Energy Loss Spectroscopy of MWNT and SWNT heated at 600 °C at 200 kV.

2. METHODS

2.1 Instrumentation

We used the HF-2200 cold field emission transmission electron microscope. Fig. 1 shows a general view of the HF-2200. We used GATAN 678 Imaging Filter for EELS analysis and a direct heating holder for specimen heating. The direct heating holder allows direct specimen mounting on its tungsten heater and permits stable high resolution microscopy.

2.2 Operation

We set the beam at 200 kV and the specimen at 600°C. After preliminary electron irradiation, we performed high resolution microscopy and EELS analysis of each nano-tube. EELS spectra were acquired in an energy range of 275 ~ 320 eV.

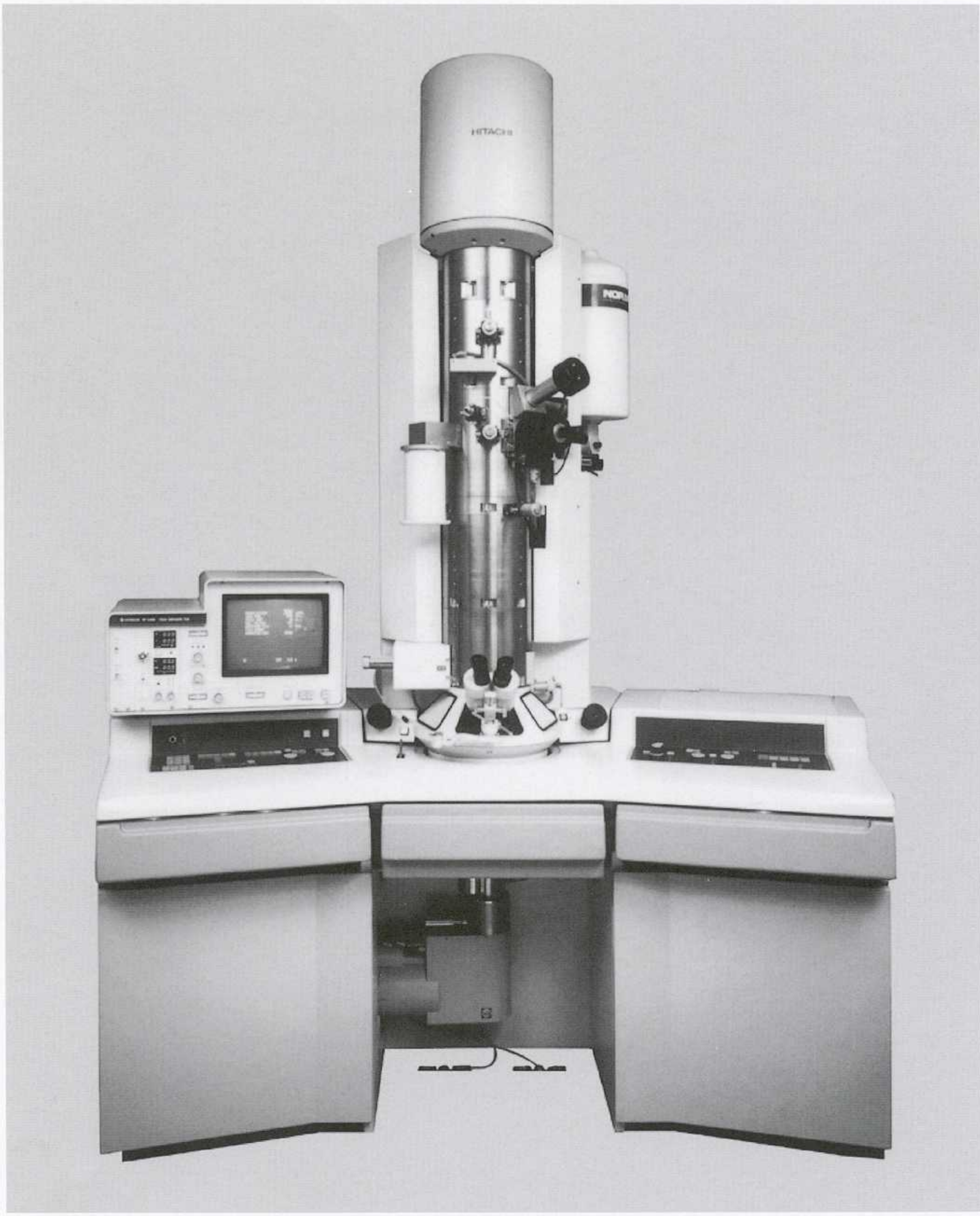


Fig. 1 A general view of the HF-2200 cold field emission transmission electron microscope

3. RESULTS OF OBSERVATION

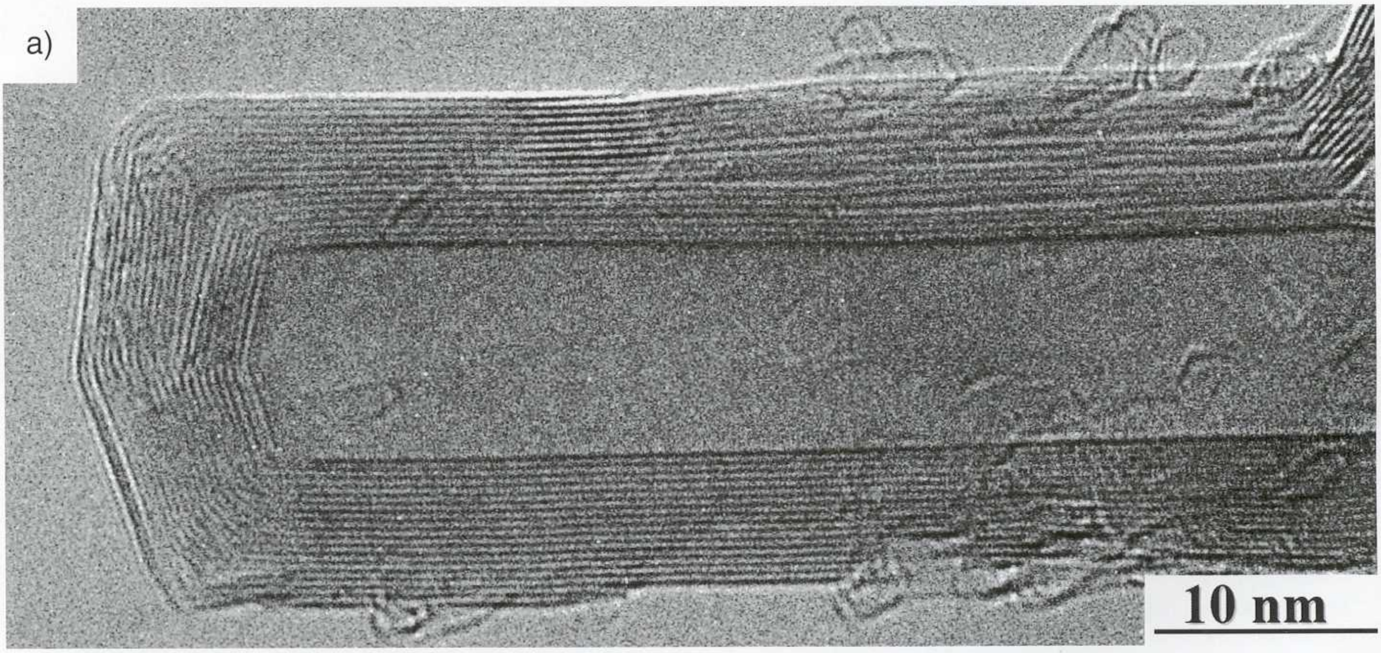
3.1 Observation and analysis of MWNT

Fig. 2 shows a high resolution image (a) and an EELS result of MWNT.

Current density of the illumination beam was 3×10^{-14} A/nm^2 and total electron dose on the specimen was about 6 × 108 e/nm^2. Observations were done at ×300,000. Signal acquisition time for EELS was 10 seconds.

By heating the specimen, contamination was removed and clean graphite structures were clearly recorded showing a crystal lattice spacing of 0.34 nm (Fig. 2a). EELS analysis (Fig. 2b) shows sharp π * and σ * peaks clearly.

a)



b)

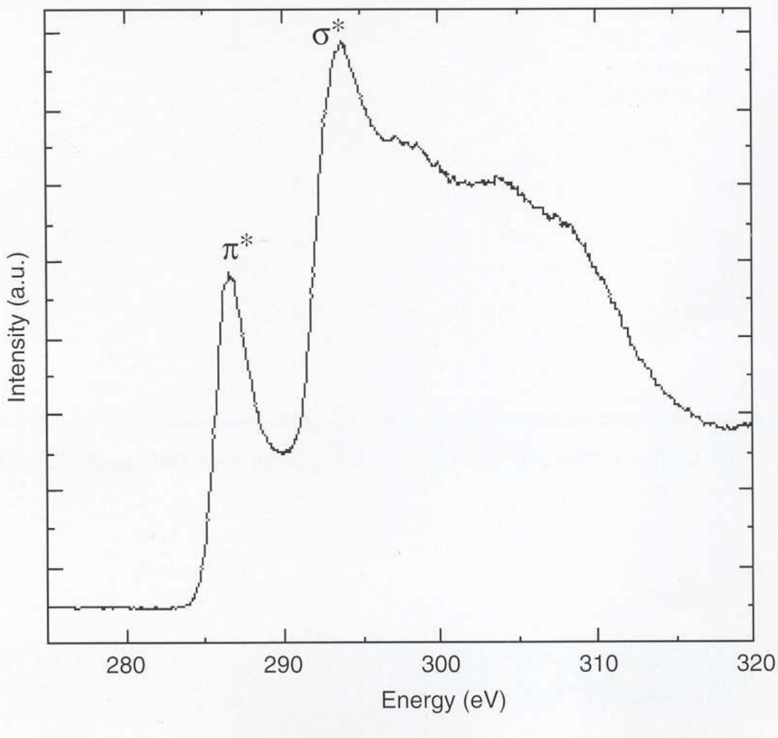
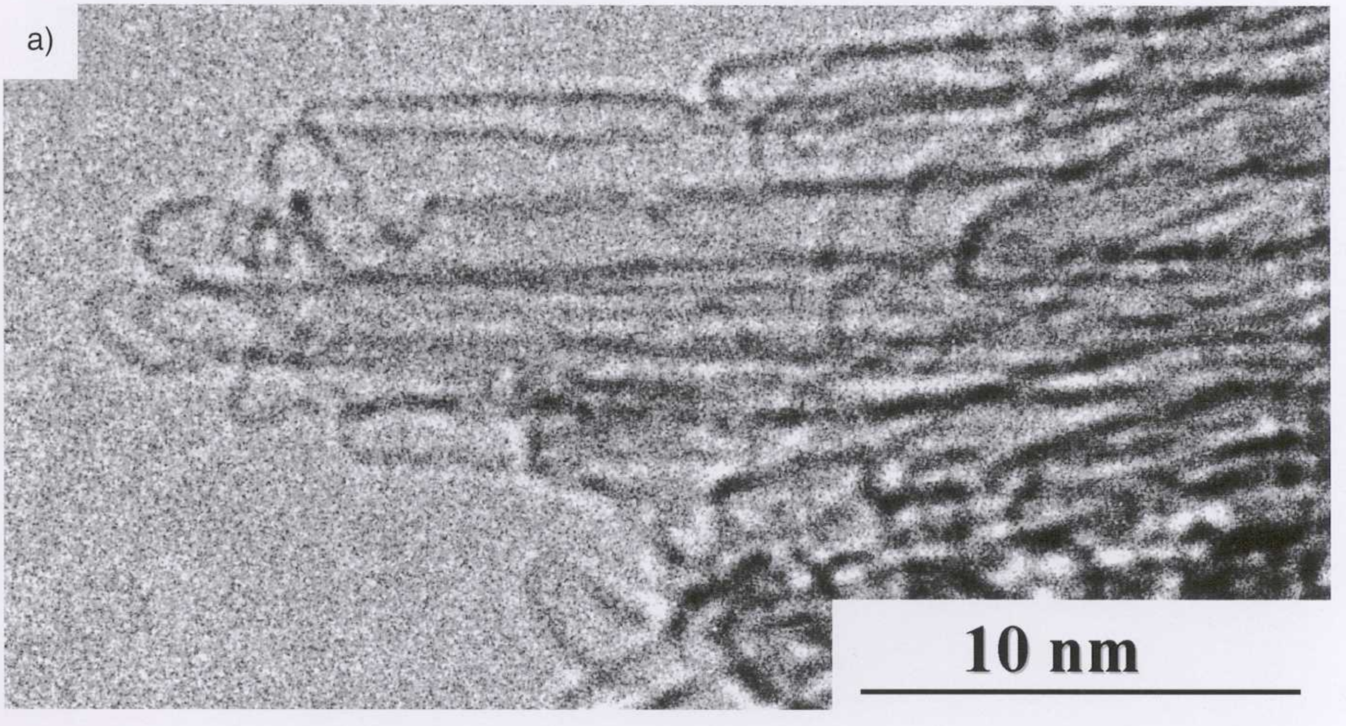


Fig. 2 A high resoon image (a) and an EELS result (b) of MWNT.

3.2 Observation and analysis of SWNT

Fig. 3(a) shows an image of a bundle of the thinnest SWNT of 1 ~ 1.5 nm in diameter. Observations were done at ×200,000. Current density of the illumination beam was 1.5 × 10^{-14} A/nm^2 and total electron dose on the specimen was about 3 × 108 e/nm^2. It shows a cap of the tube and graphene very clearly. Fig. 3(b) shows an EELS spectrum of SWNTs. For acquiring sufficient signals, total electron dose on the specimen was 1 × 109 e/nm^2 which was about twice the dose used for MWNT. The acquisition time was 2.5 minutes. The spectrum shows π * and σ * peaks indicating fine structures of SWNT clearly.

a)



b)

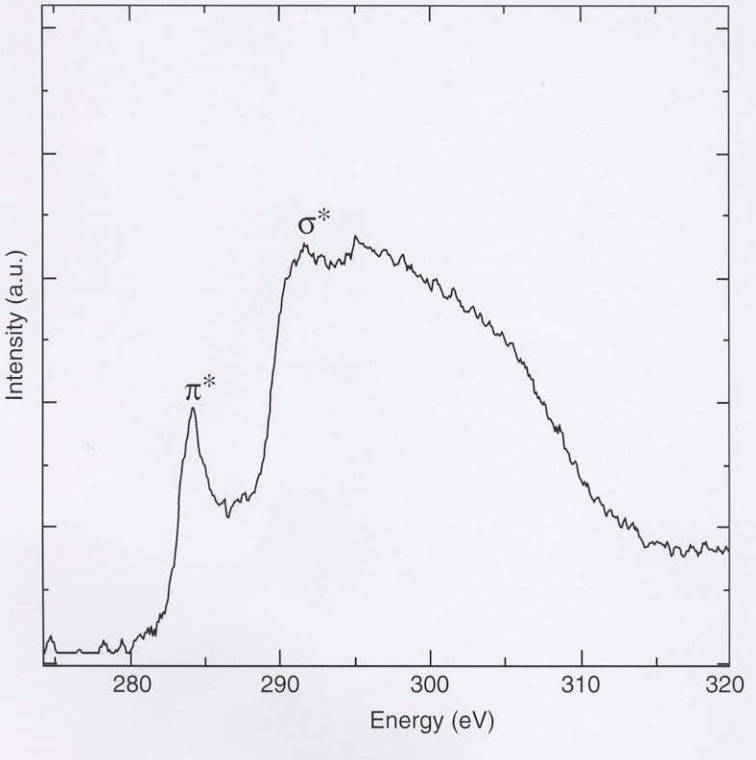
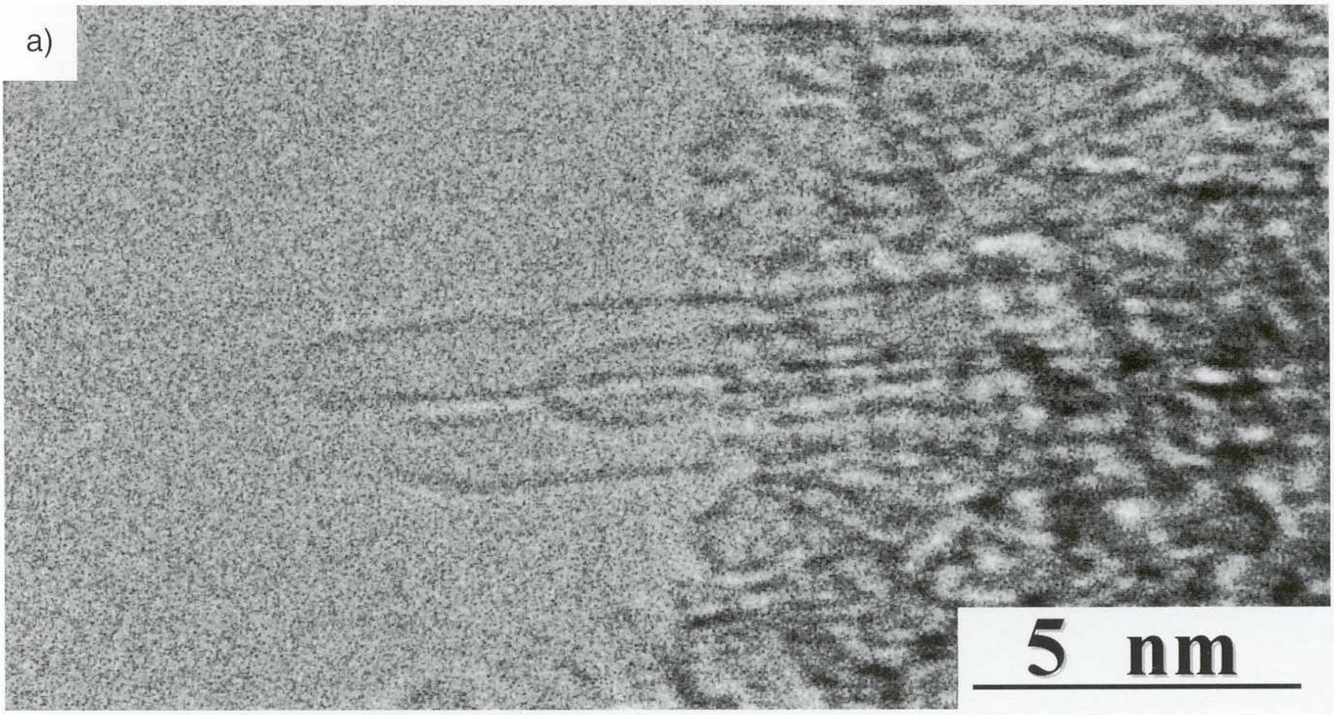
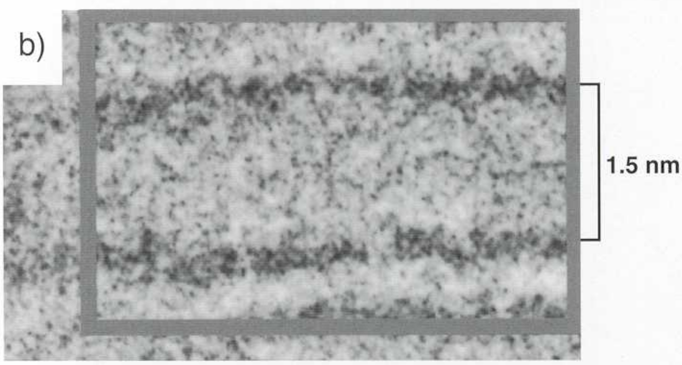


Fig. 3 A high resolution image (a) and an EELS result (b) of SWNTs.

Fig. 4(a) shows high resolution images of isolated SWNT. Observations were done at ×200,000. Current density of the illuminating beam was 1.5×10^{-14} A/nm^2 and total electron dose on the specimen was about 3 × 108 e/nm^2. We analyzed one of the tubes in Fig. 4(a). Fig. 4(b) shows the field of view. Fig. 4(c) shows an EELS spectrum. For acquiring signals from one tube, we increased the total electron dose to 8.7 × 109 e/nm2 about 15 times higher than that used for MWNT or about 9 times higher than that used for bundle-SWNT. The acquisition time was 10 minutes. The spectrum shows π * and σ * peaks indicating fine structures of SWNT.





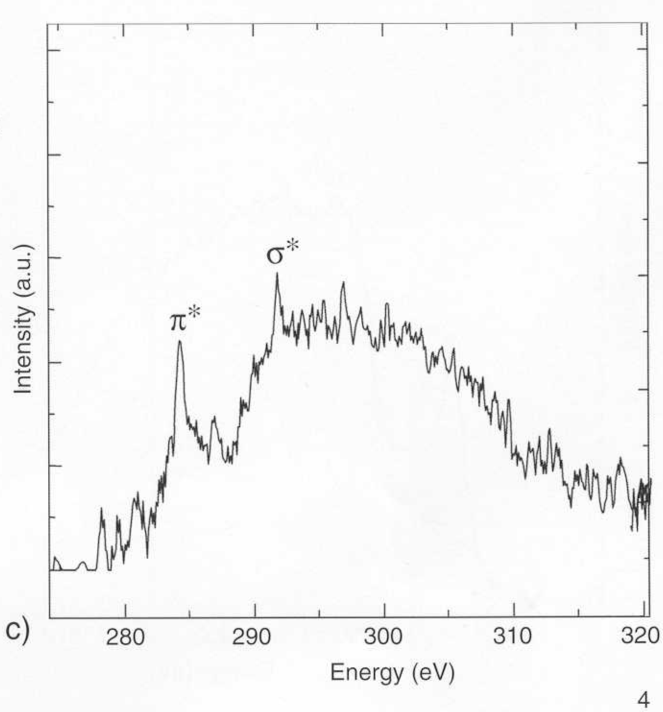


Fig. 4 A high resolution image (a), a field of view for EELS analysis (b) and an EELS spectrum (c) of isolated SWNT.

4. CLOSING REMARKS

We reported on high resolution microscopy and EELS analysis of carbon nano-tubes at high temperatures and at 200 kV. The HF-2200 cold field emission transmission electron microscope coupled with a direct heating specimen holder allows stable high resolution microscopy of carbon nano-tubes, which are sensitive to electron beam irradiation, for about one hour at 200 kV. This combined system also allows EELS operation, thus permitting chemical shift analysis. We trust that this combined system will be useful for the study of carbon nano-tubes which will be more important in the future.
We wish to thank Prof. Kazuyuki Tohji, Department of Geoscience and Technology, Tohoku University, Japan for providing samples and giving technical assistance.

5. REFERENCES

1) Saito, Y., Hamaguchi, K., Hata, K. , Uchida, K. Tasaka, Y. Ikazaki, F. Yumura, M., Kasuya, A. et. Al. : Nature, 389, 554-555 (1997)
2) Tans, S.J., Vershueren, A.R.M., Dekker, C.: Nature 393, 49-52(1998)
3) Tsukagoshi, K., Alphenaar, B.W., Ago, H.,: Nature 401, 572-574 (1999)
4) Ugarte D: Nature 359: 707-709 (1992)
5) Banhart F and Ajayan P M: Nature 382: 433-435 (1996)
6) Iijima, S.: Nature, 354, 54 (1991)
7) Iijima, S. and T. Ichihashi: Nature, 363, 603 (1993)

Instruments, Hitachi, Ltd.
Tokyo, Japan
www.hitachi.co.jp/Div/keisokuki

For further information, please contact your nearest sales representative.

Printed in Japan (H) **EX-E850-114** 2001.7