The 40 Years of High Resolution Conventional Transmission Electron Microscopy of Materials Science

Sumio Iijima[1*, 2, 3, 4]

[1*] Faculty of Science and Technology, Meijo University, Nagoya, Japan iijimas@meijo-u.ac.jp
[2] National Institute of Advanced Industrial Science and Technology / Nanotube Research Center, Tsukuba, Japan
[3] SAINT / Sungkyunkwan University, Seoul, Korea
[4] NEC Corporation, Tsukuba, Japan

Electron microscope is meant to be an instrument to characterize atomic structures of materials and so many researchers devoted their effort toward this goal. The efforts have been going even since after its invention in the 1930s.

I have published in 1971 the first high resolution electron micrograph of a titanium-niobium oxide crystal $Ti_2Nb_{10}O_{29}$ which showed positions of individual rows of the metal atoms in a projection of the crystal (Fig. 1)[1]. The picture was recorded at 100KeV under the Scherzer optimum focus condition with a special resolution of about 0.38nm. It was a beginning of the real high resolution conventional electron microscopy (HRCTEM or HRTEM) of materials although a micrograph showing individual rows of organic molecules of Cu-phthalocyanine crystal has been reported with a resolution of about 0.7nm so that it could not resolve individual atoms. The new TEM imaging method rapidly spread into a traditional diffraction contrast electron microscopy and was utilized in a wide range of materials sciences including mineralogy [2]. The semiconductor industry had a great benefit from this new TEM characterization in order to solve materials problems with semiconductor device development. One of tricks to achieve the high performance of the HRTEM was to use “a pointed filament” that is not a field emission electron source but still thermionic but because of a so small emission area comparing with a conventional hair-pin type filament it provided a brighter emission which allowed me to correct astigmatism by directly looking at the carbon granular image on the fluorescence screen at higher than 250,000 times. Another technique that I have brought was a new goniometer which was essential for working on crystalline materials. Successful imaging of single metal atoms in “bright field mode” was another break-through of HRTEM application. Interestingly for this study I have used “graphene” films as a substrate film for supporting isolated atoms of tungsten [3]. One of unique use of HRTEM was for a dynamic observation of gold clusters where the movement of individual gold atoms and structural instability of such nano-crystal were recorded on video [4]. Interestingly the observation of the gold nano-crystals has initiated the present prosperity of gold catalyst [5].

From time to time carbon materials appeared in HRTEM study since the thin amorphous carbon films are commonly used as TEM specimen support films as well as glassy carbon chips with 0.34nm lattice spacing for testing the resolution of the instrument for the optics alignment [6,7]. The atomic structural details of these carbon materials that I have found of interesting were responsible for the discovering of carbon nanotubes in 1991(Fig. 2) [8]. The latest study of the carbon nanotubes and related materials will be introduced here also (Fig. 3). My interest of HRTEM covered thin bulk films (three-dimension), nano-crystals (quasi-zero-D) and carbon nanotubes (one-D). I have also spend some years to develop to study surface atomic structures of Si by building a ultra-high vacuum

HRTEM instrument which required instrumental development of high-resolution capability and achieving UHV operation [9]. With this I thought my challenge to HRTEM studies of materials of various morphologies covering all dimensions from one-D to three-D structures has completed but it has not been finished yet, which will be described below.

Lastly I should mention briefly the latest HRTEM of materials with real Zero-dimension which deal with imaging of individual atoms and molecules. The works have been done mostly using carbon nanotubes as a specimen support because they are almost transparent and thus perfectly ideal for the present purpose [10,11,12]. Emphasis will be on the Cs corrected TEM with energy-filtered imaging facilities of EELS technique.

References

[1] S.Iijima, *J. Appl. Phys.*. 42 (2002) 5891.
[2] M. A. O'Keefe, P. R. Buseck and S. Iijima, *Nature*, 274, (1978) 322.
[3] S. Iijima, *Optik*, 48, (1977) 193.
[4] S. Iijima and T. Ichihashi, *Phys. Rev. Lett.*, 56, (1986) 616.
[5] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 115, (1989) 301.
[6] S. Iijima, *Chemica Scripta*, 14, (1978-9) 117.
[7] S. Iijima, *J. Cryst. Growth*, 50, (1980) 675.
[8] S. Iijima, *Nature*, 354, (1991) 56.
[9] E. Bengu, et al., *Phys. Rev. Lett.*, 77, (1996) 4226.
[10] K. Suenaga, et al., *Nature Nanotech.*, 2, (2007) 358.
[11] Z. Liu, et al., *Nature Nanotech.*, 2, (2007) 422.
[12] C. H. Jin, et al., *Phys. Rev. Lett.*, 102, (2009) 205501 (1).

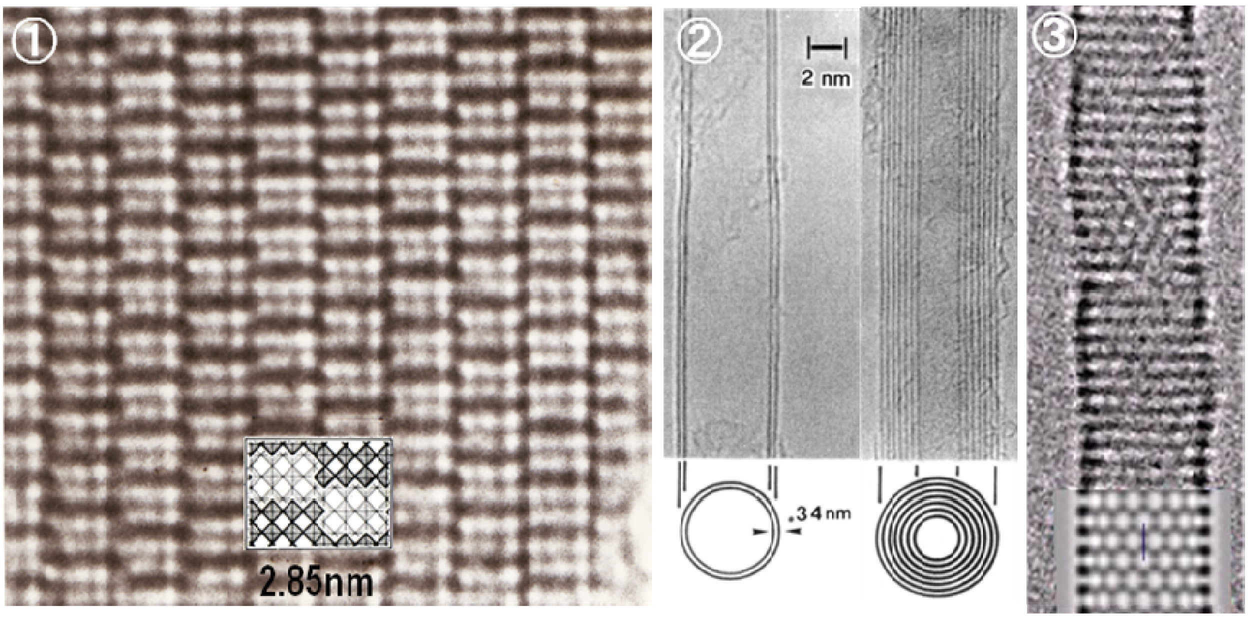

Fig. 1. ① The first HRTEM image of a crystal of $Ti_2Nb_{10}O_{29}$ showing individual rows of metal atoms separated by 0.38nm in a projection along the c-axis, which was reported in 1971[1]. ② A HRTEM images of multi-wall carbon nanotubes reported in Nature in 991[8]. ③ A recent HRTEM image of a single wall carbon nanotube showing arrays of carbon atoms [10].