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TEM Study of Carbon Nanotubes

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INTRODUCTION

High resolution transmission electron microscopy (HRTEM) has been intensively used in characterization of crystalline defects, and it can provide 3-D structural information in some cases. For example structural instability of nanometersized metal particles were found in the real time VTR observation at the atomic level resolution (Iijima et al. 1986). Such low dimensional structures are of rccent interest among solid state scientists who expect novel properties not found in bulk forms. More recently discovery of C_{60}, or the fullerene, has brought a great excitements in interdisciplinary fields of science and technology (Kroto et al. 1985). The individual C_{60} molecule, which is a graphitic shell structure consisting of 60 carbon atoms, and 0.7nm in diameter, can be imaged without difficulty be HRTEM. Many of fundamental problems with the molecule however are not solved by HREM. On the other hand, carbon nanotubes, a family of fullerenes and discovered serendipitously by the present author (Iijima 1991), are an ideal subject for the HRTEM investigation and in fact their structures can only be analyzed by this technique. The present talk is concerned with carbonaceous materials and nanotubes with an emphasis of unique use of the HRTEM.

GRAPHITIC STRUCTURES OF CARBON

Three forms of carbon, namely, diamond, graphite and amorphous carbon, are well known and their structures have been studied intensively be HRTEM. Graphitic structures vary from an amorphous state to a perfect graphite crystal depending upon their thermal treatments during the specimen preparation. Partially graphitized carbon is familiar to electron microscopists for the microscope resolution test specimen (c-spacing 0.34nm). The present author found spherical graphite particles of a nanometer size in a vacuum deposited amorphous carbon films (Iijima 1980). The particle consists of nesting spherical shells of graphitic sheets (Fig. 1). The most inner shell is about 0.7nm in diameter and close to the size of a C_{60} molecule (Iijima 1987). Growth of such a multishell structure is a key to understand the C_{60} molecule formation (Kroto 1988).

MULTI-SHELL CARBON NANOTUBES

Search for the multi-shell graphite particles leads to unexpected discovery of carbon nanotubes which grow on a cathode in a carbon-arc chamber for the C_{60} production (Iijima 1991). HRTEM images of carbon nanotubes tell us their diameters and the number of shells (Fig. 2a). The fact that basal plane lattice images

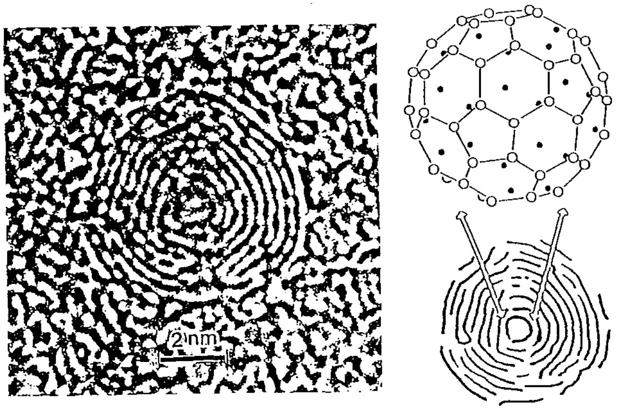

Fig. 1. A HRTEM image of a carbon particle of multi-shelled spherical shape. The most inner shell diameter is 0.7nm, corresponding to the size of the C_{60} molecule (indicated in the illustration).

are always seen independently in the tubule orientations suggests that the graphitic shells are nesting tubes rather than a scroll. In this case the HRTEM enables us to deduce tubule's 3-D structures, Cylindrical crystals are found commonly in living cells but rarely in inorganic structures. Atomic arrangements on the tubules are studied by examining their electron diffraction patterns. This was carried out by the micro-beam diffraction mode in the TEM. The method enables us to examine a tubule structure on the basis of an single atom sheet. The analysis of the diffraction patterns results in finding a helical arrangement of carbon hexagon rings on each cylinder (Fig. 2b). Helicity is a popular structure in biological substances such as micro-tubulines and a tobacco-mosaic virus.

SINGLE-SHELL CARBON NANOTUBES WITH ABOUT ONE NANOMETER DIAMETER

Electronic band structure calculations of nanotubes (Hamada et al. 1992) predict a semiconductive nature of the tubules when they are less than 2nm in diameter and single-shelled tubes. Such an ideal nanotube has been prepared successfully in a carbon-arc deposition by feeding metal catalyst (Iijima et al. 1993, Bethune et al. 1993). The thinnest

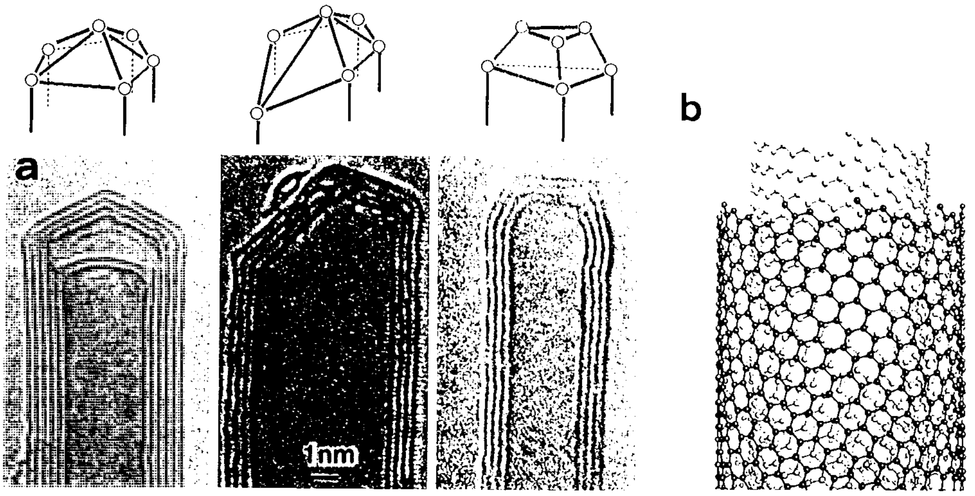

Fig. 2. (a) HRTEM images of multi-shelled carbon nanotubes with caps which contain pentgonal carbon rings as indicated by open circles in illustrations. (b) and idealized 3-D model of a nesting carbon nanotube.

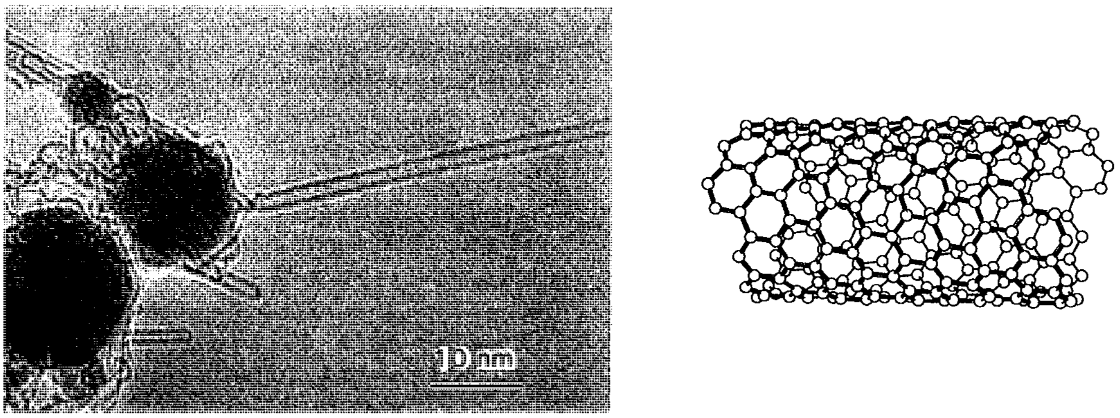

Fig. 3. A model for a single-shelled and helical carbon nanotube with a diameter of 0.9nm whose existance has been confirmed experimentally.

tubuic was only 0.7nm in diameter which is the same as that of C_{60}. An electron diffraction pattern recorded from such an individual tubule shows the 2mm symmetry, which confirms the presence of the helicity in carbon hexagon arrangements (Fig. 3). The spiral pitches are different from tublue to tubule.

MORPHOLOGY AND NON-HEXAGON CARBON RINGS

The role of pentagons in fullerene molecule structures is to introduce positive gaussian curvatures into a flat carbon hexagon network. A completely closed cage structure needs twelve pentagons according to the Euler theorem. The rule is applied equally to morphologies of tubules and their caps (Iijima et al. 1992). A variety of cap shapes are attributed to a distribution of six pentagons on the tip (Fig. 2a). A similar packing geometry is known in spherical viruses. A negative curvature which is caused by heptagons or octagons is observed often in our nanotubes. Non-hexagon carbon rings were found to be more reactive in oxidation than hexagon rings (Ajayan et al. 1993, Ajayan et al. 1993). This observation is suggestive in the characterization of activated carbon.

GROWTH OF CARBON NANOTUBES

It is needed to measure well-defined tubules in the characterization of their electronic properties since they are critically dependent on their structures. Tubule morphologies are associated with their growth and thus their analysis is important (Iijiman 1993). The effort is now in progress. Our strategy is to under-stand the growth mechanism of tubules and to control it to produce any desired morphology. In the single shelled tubule production th metal particles act as growth centers but their details need further study (Iijima 1994).

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