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An atomic force microscope study of carbon onions and related nanoparticles

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Abstract. Carbon onions are found along with carbon nanotubes and other carbon nanoparticles in the cathodic deposit in the arc-vaporization of graphite. Atomic force microscopy has been used to characterize these particles on the basis of their sizes and shapes. Onion-like particles have three-dimensional, near spherical structure and are distinct from two-dimensional graphitic particles. The spherical shape and height to diameter ratios obtained using atomic force microscope, afford a distinction between onion-like structures and other carbon nanoparticles.

Keywords. Atomic force microscopy; carbon onions; fullerenes; carbon nanotubes.

1. Introduction

During the course of investigations of fullerenes and carbon nanotubes, another novel carbon species involving concentric shells of fullerenes, popularly called onions, was discovered recently by Ugarte (1992, 1994). Onions, being hyperfullerenes, should involve concentric cage structures with six- and five-membered rings. Although, onion-like structures have been described from transmission electron microscopy (TEM) (deHeer and Ugarte 1993; Ugarte 1994; Aiyer *et al* 1995), it can be difficult to distinguish them from small polyhedral graphitic particles. The main distinction will have to come from the volume to surface ratio of these particles. Furthermore, the shape of a graphitic particle can be more two-dimensional compared to onion-like structure, which has to have a three-dimensional or near-spherical structure. Also given the fact that TEM provides the cross-sectional view of an object in a plane perpendicular to the electron beam, one cannot ideally differentiate between a TEM image of a hemispherical or polygonal cap of nanotubes from that of a spherical or polyhedral graphitic particle. Maiti *et al* (1993) argue that simulated TEM pictures show that polyhedral cages can appear spheroidal when viewed from a particular high symmetry direction, and polyhedral when viewed from a more general direction. Lu and Yang (1994) have shown that spherical multiple-shell fullerenes are likely the most stable structure of large carbon clusters. One can therefore impose certain restrictions of sizes and shapes of the nanoparticles, observed in atomic force microscope (AFM) images, to be identified as onions. A general feature of onions, that has evolved from TEM studies is that they generally consist of around 10–15 concentric shells of variable diameter. This implies that the diameter of such onions would be around 20–30 nm. We, therefore considered it instructive to investigate the shapes and morphologies of various carbon nanoparticles using AFM.

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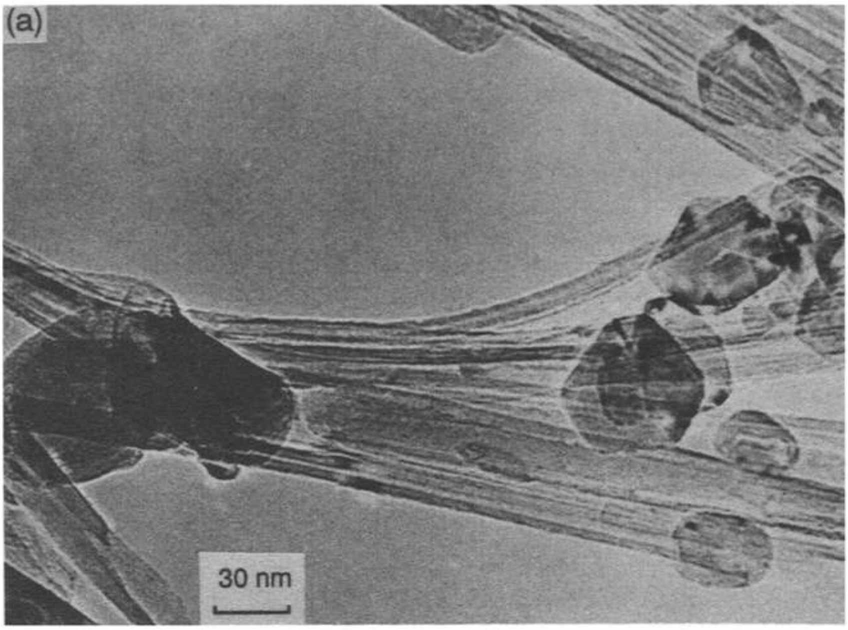
2. Experimental

Sputtered Au polycrystalline films were deposited using a POLARON sputter coater, on freshly cleaved muscovite. The surface morphology of the evaporated Au films were



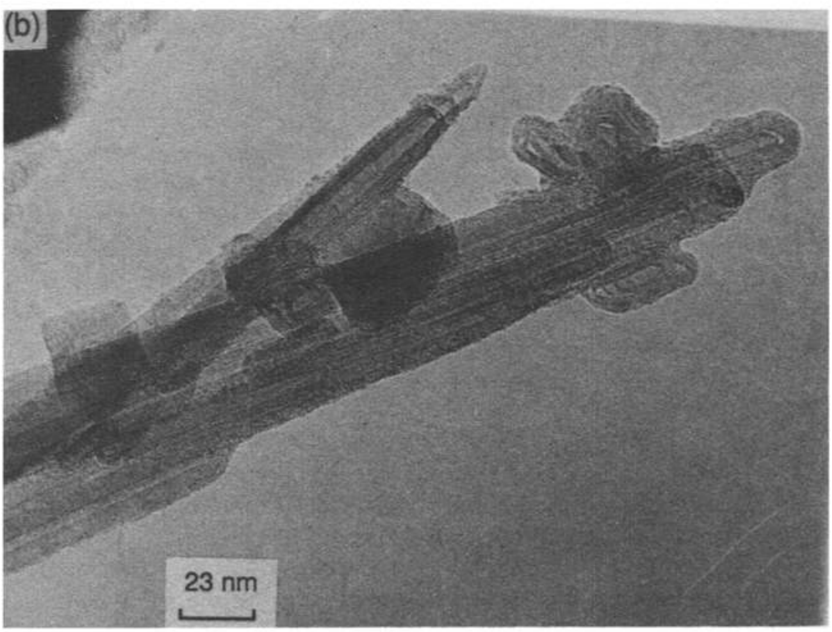


Figure 1. a-b. TEM images of onion-like structures found along with carbon nanotubes in the cathodic deposit obtained in the arc-vaporization of graphite rods.

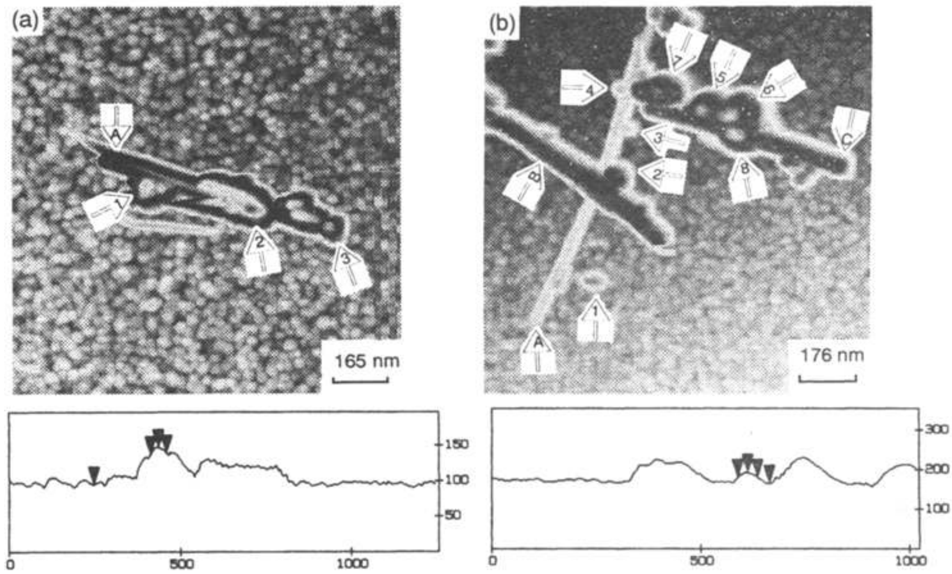


Figure 2. AFM images of carbon nanoparticles present along with carbon nanotubes. **a.** Shows nanoparticles 1, 2 and 3 present along with a nanotube A. Profile of particle 1 is shown below the image, where the diameter is 45 nm and the height is 53 nm and **b.** nanoparticles (1–8) present along with three nanotubes A, B and C. Section profile of particle 3 is shown below, where the diameter is 50 nm and height is 27 nm. The x- and y-axes scales of the profiles in this and all subsequent figures are in nm.

examined using atomic force microscopy (AFM) and scanning tunneling microscopy (STM). AFM revealed nearly spherical Au grains of 40–50 nm in diameter and a roughness of about 7 nm. STM revealed smaller particles of about 15–17 nm in diameter, within these grains.

The core portion of the cathodic stub, obtained in the arc-vaporization of graphite rods, comprises of nanotubes and other graphitic particles. This powder was cleaned by heating in O_2 at 480°C for 12 h. Drops of the suspension of this powder in CCl_4 were let to evaporate on the Au film.

A Nanoscope II, contact-mode AFM was used to characterize the surface morphology of carbon nanotubes and graphitic particles, in air. All the images shown here, were captured in the constant force mode, with an imaging force of the order of 10^{-9} Newtons.

3. Results and discussion

Onions are generally found along with carbon nanotubes as evidenced in the TEM images of nanotubes as shown in figure 1. In the light of this observation, we first examined the AFM images of carbon nanoparticles present along with carbon nanotubes. In figure 2, we show typical AFM contour plots of onion-like structures accompanying the nanotubes. For example, in figure 2a, we identify three particles designated 1, 2 and 3 which have diameters in the range of 40–70 nm. The heights of

Table 1. Dimensions of nanoparticles in figure 2.

Figure	Particle #	x-y Dimension ('D' nm)	Height ('H' nm)	H/D	Description
2(a)	1	45	53	1·2	Spherical
	2	50 × 36	59	1·2	Polyhedral
	3	69 × 36	44	0·6	Polyhedral
2(b)	1	87 × 50	32	0·4	Polyhedral
	2	52	55	1·1	Spherical
	3	54	27	0·5	Spherical
	4	59	35	0·6	Spherical
	5	69	33	0·5	Spherical
	6	97 × 87	29	0·3	Polyhedral
	7	118 × 72	46	0·4	Polyhedral
	8	66 × 50	51	0·8	Polyhedral

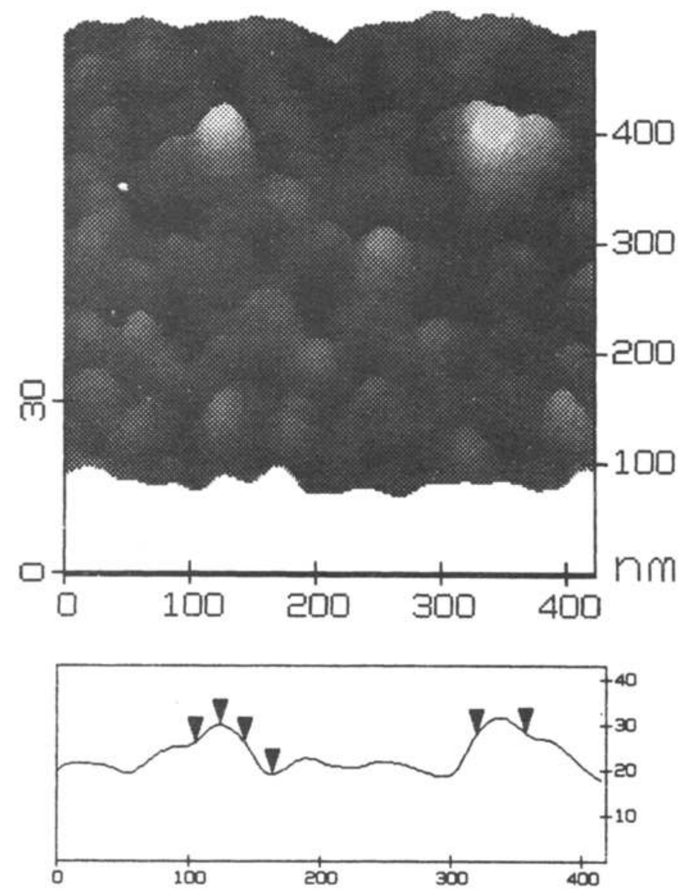


Figure 3. Surface plot of two isolated onion-like particles, with the section profile across them shown below, where the diameters are 37 nm each and the height is 11 nm.

these particles vary between 40–60 nm. Of these, particle 1 is closest to being spherical and may be considered to be onion-like. The line profile across particle 1 shown below the image, supports this conclusion. In figure 2b, we see the presence of a large number of onion-like particles with three nanotubes. Particles marked 1–6, all have characteristic diameters in the range of 50–90 nm and heights in the range of 30–50 nm. We show a line profile of particle 3 in the figure. Particles 2–5 are close to being spherical. Compared to these, particles 7 and 8 are considerably larger, with x-y dimensions of around 120 nm × 70 nm and with heights in the 30–40 nm range, suggesting that they are unlikely to be onions. In table 1, we list the dimensions of the various particles.

In addition to onion-like carbon nanoparticles found along with nanotubes, we have imaged a number of isolated carbon nanostructures, some of which are fairly spherical. Their sizes vary widely. We briefly describe the morphology of these carbon nanoparticles. In figure 3, we show the surface plot of an AFM image showing two isolated particles whose diameters are 37 nm each and heights of 11 nm and 12 nm, which are not far from onion-like structures. We have imaged particles still larger than those in figure 3, some of which are spherical. We cannot, however, be certain that they are onion-like since the height to diameter (H/D) ratio is much smaller than one would expect for onions.

In figure 4a, we show an image along with the line profile of a particle whose diameter is 290 nm, which appears to be spherical but the height is only 40 nm. In figure 4b, we see a large spherical arrangement consisting of a large particle along with small spherical particles whose diameters are around 70 nm and height 35 nm, which are quite onion-like. This may suggest occurrence of packing of the onion-like particles. Ru *et al* (1996) have demonstrated that carbon onions formed in TEM also show some aggregation phenomenon. These images are compared with those of polyhedral particles which do not show any apparent spherical shape. In figure 4c, we show an AFM contour plot of two polyhedral particles. The line profile across these two particles along one direction gives the diameters to be 230 nm and 250 nm, with heights of 101 nm and 124 nm, respectively. Table 2 lists the dimensions of the various particles in figure 4.

4. Conclusions

We have studied the shapes and sizes of different carbon nanoparticles obtained in the arc-vaporization of graphite rods, using AFM. Particles for which the H/D ratio is greater than 0·3 are considered to be three-dimensional structures and those with less than 0·3 are considered to be two-dimensional or planar structures. Particles with distinct x-y dimensions are considered to be polyhedral *vis-a-vis* those with similar x-y dimensions are considered to be spherical. We find three types of carbon nanoparticles.

Type 1: This type of nanoparticles occur along with or attached to nanotubes and have typical sizes in the range of 40–70 nm. Most of these particles are spherical or near-spherical in shape with the height to diameter ratios of greater than 0·3. Such particles can be identified as carbon onions because of their reasonably small size and three-dimensional shape.

Type 2: These are isolated particles with diameters in the range of 30–40 nm and heights in the range of 10–12 nm. The height to diameter ratio is around 0·3 and hence, they are not far from onion-like structures.

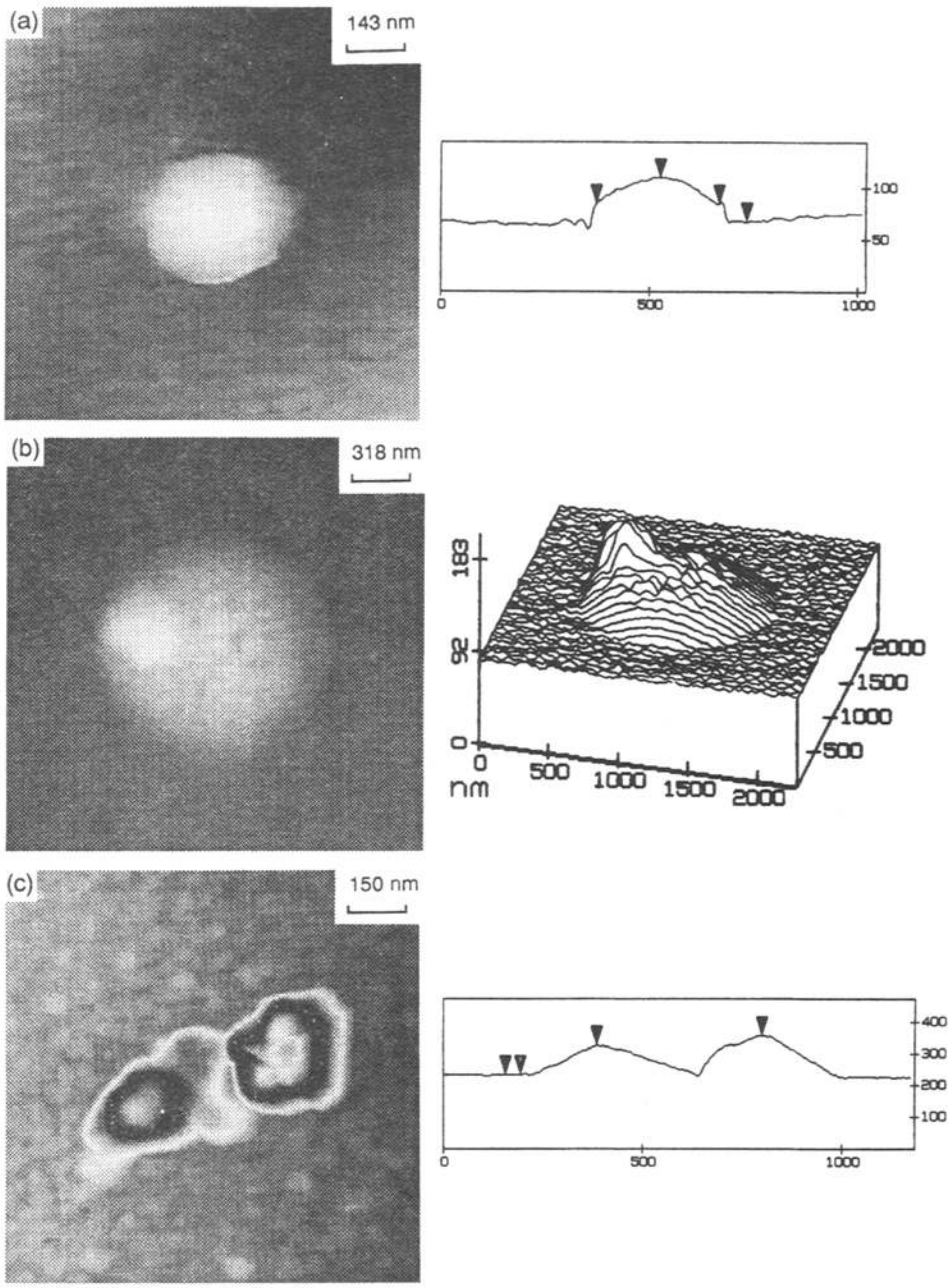


Figure 4. AFM images of large carbon nanostructures. **a.** Top-view of a large spherical structure with section profile shown alongside, where the diameter is 294 nm and height is 44 nm, **b.** image showing a large and several small particles arranged in a spherical shape. A lineplot is shown on the side and **c.** contour plot of two non-spherical particles with a line profile across them, giving heights of 101 nm and 124 nm, respectively.

Table 2. Dimensions of nanoparticles shown in figure 4.

Figure	Particle #	x-y Dimension ('D' nm)	Height ('H' nm)	H/D	Description
4(a)	1	290	40	0·1	Planar
4(b)	1	926	53	0·1	Planar
	2	72	31	0·4	Spherical
4(c)	1	251 × 171	101	0·4	Polyhedral
	2	254 × 232	124	0·5	Polyhedral

Type 3: These are very large particles with diameters typically around 250 nm and their shapes are either spherical or polyhedral. These large particles may be an agglomeration of smaller spherical or polyhedral particles, as revealed sometimes in the AFM images. We observed a very large spherical particle with a diameter of ~920 nm which is an agglomerate of small onion-like particles.

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