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SHORT TECHNICAL NOTE

Carbon nanotubes and other graphitic structures as contaminants on evaporated carbon films

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Summary

Evaporated carbon support films for transmission electron microscopy (TEM) often contain fullerene-like structures such as nanotubes and nanoparticles. This could cause serious confusion in TEM studies of fullerene-related carbons. Other, poorly graphitized, particles are also frequently seen.

Introduction

High-resolution electron microscopy (HREM) has been widely used in studies of fullerene-related carbons, and in particular has been applied extensively to the study of carbon nanotubes (Iijima, 1991; Ebbesen & Ajayan, 1992) and carbon nanoparticles (Harris *et al.*, 1993; Saito *et al.*, 1993). The purpose of this Note is to draw the attention of workers in this field to the fact that carbon nanotubes, nanoparticles and other graphitic carbon structures are sometimes present as contaminants on transmission electron microscope (TEM) support films. This could be a major cause of confusion in fullerene studies. Serious errors could arise, for example, in studies aimed at exploring new methods for nanotube synthesis.

Experimental

The present study involved examining 10 unused evaporated carbon films supported on copper grids, obtained from two different suppliers. Three types of carbon film were examined: 'lacey', 'holey' and continuous. The microscope employed was a Philips CM20 TEM operated at 200 kV. Carbon nanotubes, nanoparticles or other graphitic carbon structures were found to be present as contaminants on all of the grids examined. The amount, and nature, of these contaminants varied considerably from grid to grid; in some cases large clusters of nanotubes and nanoparticles could be found quite easily, while in others only isolated nanoparticles and other structures were seen. Figure 1 shows a typical cluster of nanotube-containing material found on a lacey carbon film. Close examination of such regions showed them to be made up almost exclusively of graphitic nanotubes and nanoparticles. Higher magnification images of two regions from a different lacey film are shown in Fig. 2. As can be seen in Fig. 2(a), the tubes could sometimes be greater than 1 μm in length. High-resolution images showed that the tubes were invariably multilayered, and capped at both ends, as observed in nanotubes prepared by the conventional arc-evaporation method. Typical high-resolution images are shown in Fig. 3. In these images the structure of the individual layers appears somewhat less perfect than in tubes prepared by conventional arc-evaporation, and it can be seen that the tubes have a thin surface coating of amorphous material.

In addition to nanotubes and nanoparticles, other graphitic carbon structures were frequently found on the support films. Commonly observed were relatively large, hollow bodies such as those shown in Fig. 4. These could be either globular (Fig. 4a) or tube-like (Fig. 4b). High-resolution imaging showed that the walls of these objects were partially graphitized, but the overall structures were much less well defined than the smaller nanotubes or nanoparticles. Similar structures have been discussed by Rietmeijer (1985). Occasionally, thin hexagonal platelets were also seen on the carbon films, as noted previously by Ando (1995). These did not appear to be graphitic but were apparently crystalline. Ando has suggested that they may be crystals of carbyne, i.e. *sp*-bonded carbon.

X-ray microanalysis indicated that there were traces of silicon on the carbon films. Spectra recorded from the graphitic contaminants were no different from those recorded from uncontaminated areas.

Discussion

A variety of techniques are used to prepare carbon support films for transmission electron microscopy (Goodhew, 1972), but they all involve, at some stage,

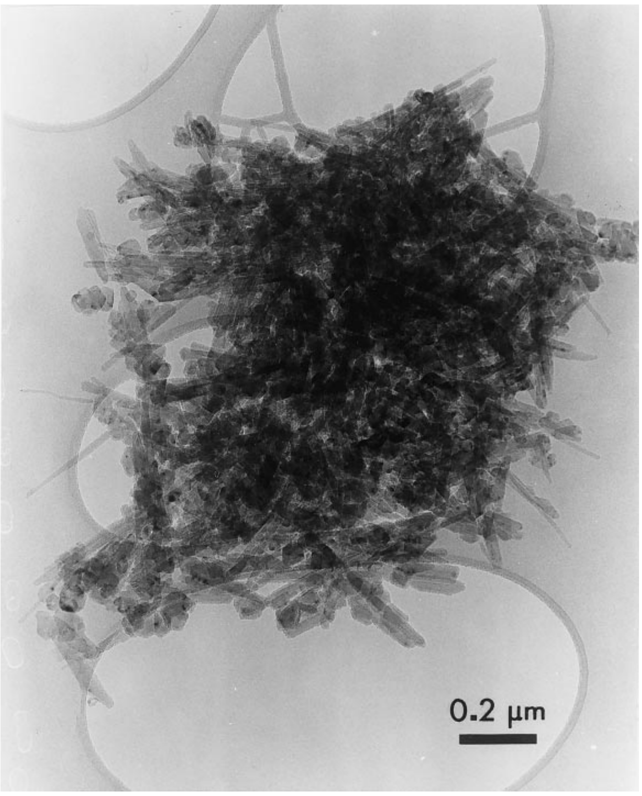

Fig. 1. Cluster of nanotubes and nanoparticles on lacey carbon support film.

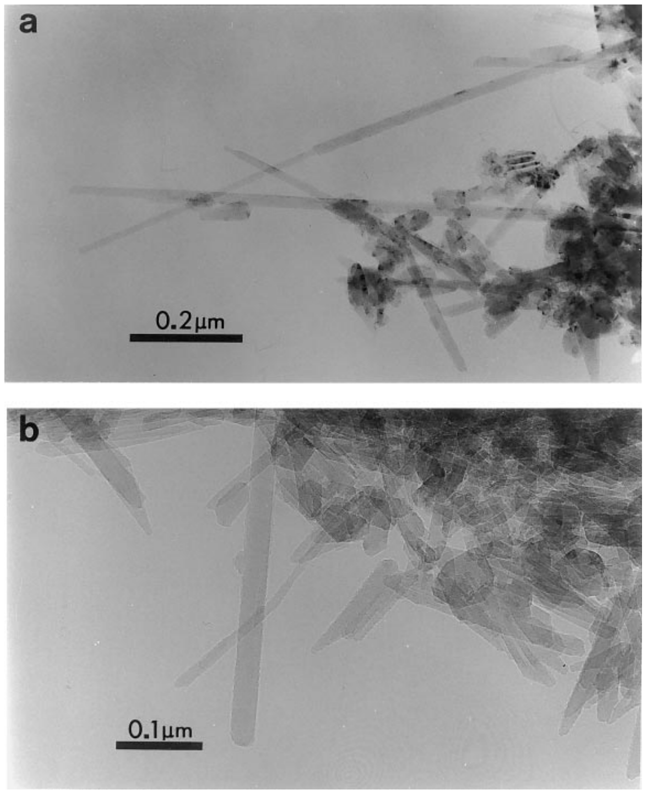

Fig. 2. Higher magnification images of nanotube/nanoparticle clusters.

the arc-evaporation of graphite. It is therefore not too surprising that fullerene-related structures are present, since arc-evaporation is also the favoured method for preparing fullerenes and nanotubes (Krätschmer *et al.*, 1990; Iijima, 1991). The only significant difference between the two processes is that an atmosphere of helium rather than a vacuum is employed in the arc-evaporation vessel for fullerene synthesis. It is also worth recalling that some of the earliest observations of nanotube-like structures were made by Iijima in studies of evaporated carbon films very similar to those used as support films (Iijima, 1980a,b).

The other, less well-defined, graphitic structures observed on the carbon films are unlikely to be a result of arc-evaporation, but probably originate from an earlier stage of the production process, as discussed by Rietmeijer (1985). In the preparation of holey films, the first stage usually involves the casting of a plastic film, which contains a fine dispersion of an immiscible liquid to create the holes. Some recipes require that the plastic film is then heated at temperatures around 1000 °C (e.g. Fukami & Adachi, 1965), and it is during this stage that the poorly graphitized particles may form, as a result of partial fracturing and carbonization of the thin polymer film.

The presence of unusual graphitic contaminants on TEM

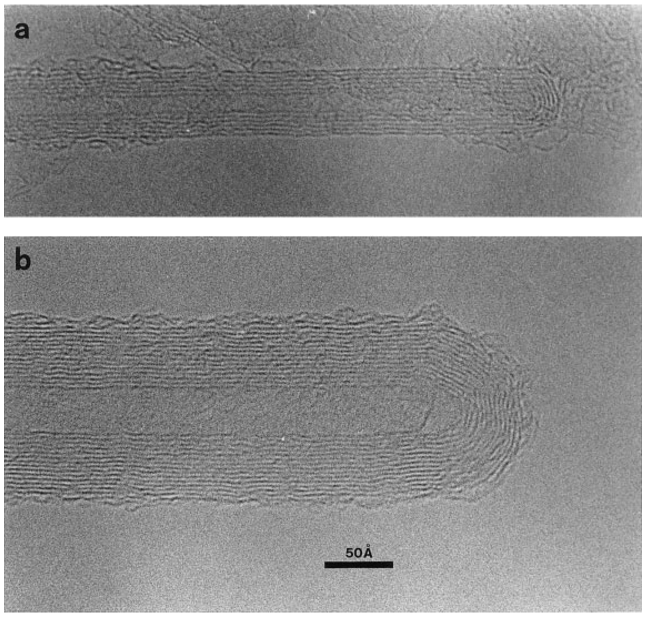

Fig. 3. High-resolution images showing typical carbon nanotubes in the tip region.

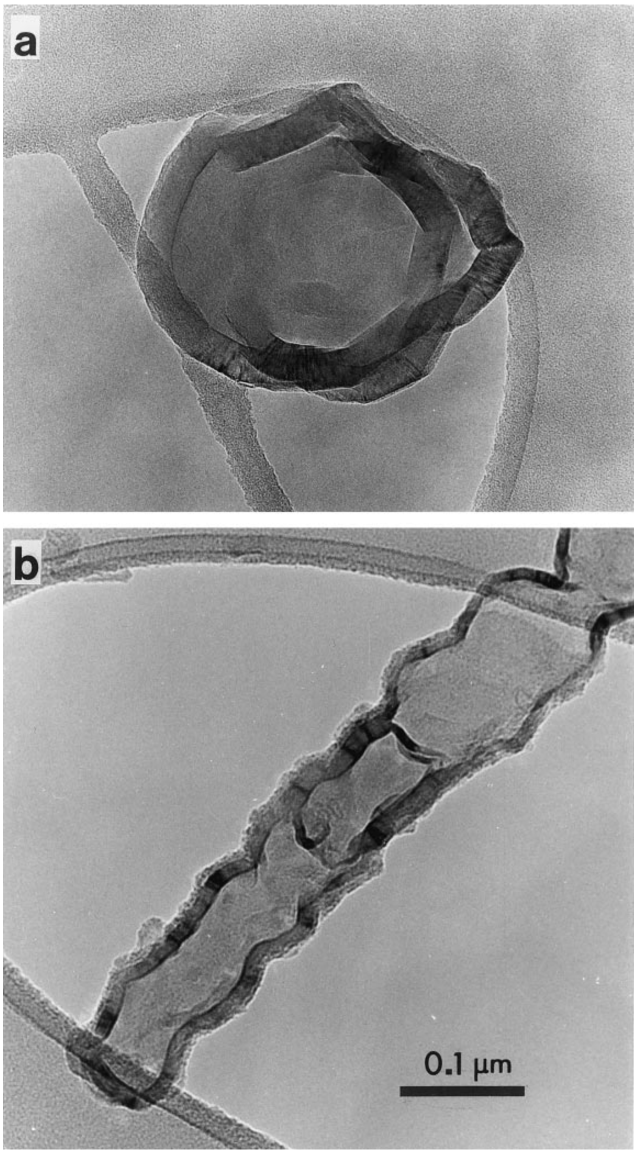

Fig. 4. Hollow, poorly graphitized structures observed on holey carbon film.

support films has been noted by workers on carbonaceous meteorites (Rietmeijer, 1985) and diamond (T. Evans, personal communication), but does not appear to be widely appreciated in the fullerene community. Thus, there are examples in the fullerene literature where these contaminants have almost certainly been mistaken for sample material. In order to avoid such pitfalls, the support films should ideally be examined before depositing any sample material, in order to check their purity. Alternatively, noncarbon support films, such as those made from silicon monoxide, could be used.

Finally, the observation that nanotubes and related structures are formed in evaporated carbon films may in itself be of interest. In the Iijima–Ebbesen–Ajayan method for nanotube synthesis, the nanotubes and nanoparticles are found only in the deposit which forms on the negative electrode after arcing, and are not found in the soot which deposits on the walls of the arc-evaporation vessel. The mechanism whereby nanotubes and particles can form in an evaporated carbon film may be worthy of further study.

Acknowledgment

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