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Carbonaceous contaminants on support films for transmission electron microscopy

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Abstract

Evaporated carbon support films for transmission electron microscopy often contain carbonaceous contaminants. These include poorly graphitized carbon, fragments of graphite, and fullerene-like structures such as nanotubes and nanoparticles. In some cases, carbyne crystals may also be present. There are many examples in the carbon literature where these contaminants have been mistaken for sample material. This paper describes the kinds of contaminants observed on grids obtained from a number of commercial suppliers.

Keywords: A. Carbon nanotubes, Carbyne, Graphite; C. Transmission electron microscopy

1. Introduction

Samples for transmission electron microscopy (TEM) are frequently supported on evaporated carbon films attached to metal grids. It is generally assumed that such films are clean and uncontaminated when obtained from the supplier, but this is actually far from the case. Almost invariably a range of contaminant particles, mostly carbon-containing, can be found on the support films. Needless to say, this can cause considerable confusion in TEM studies of carbon materials. Two fields which have been particularly affected are studies of fullerene-related carbons and studies of carbonaceous material extracted from meteorites. The aim of this paper is to describe some of the carbonaceous contaminants which are found on TEM support films, and to point out examples from the literature where these contaminants have almost certainly been mistaken for sample material.

2. Experimental

The carbon films examined in the present study were obtained from four different suppliers: two in the UK (Agar Scientific, Taab), one in the USA (SPI) and one in Japan (Oken Shoji; type B grids). The films were either continuous, ‘‘holey’’ or ‘‘lacey’’, and were supported on copper or nickel grids. Care was taken to ensure that the grids were not exposed to dust or other contamination between removal from packaging and loading into the microscope. In addition to bright field imaging, energy dispersive X-ray (EDX) microanalysis of contaminant particles was carried out.

3. Results

The grids obtained from Agar, Taab and SPI were generally very similar, so these will be considered first. Carbonaceous contaminants were present on all of the grids examined, and two of the most commonly observed types are shown in Fig. 1. The material shown in Fig. 1(a) consists of a crumpled sheet of poorly graphitized carbon; this kind of contamination has been discussed previously by Rietmeijer [1]. The particles of sheet-like material could be several micrometres in size, and high resolution imaging confirmed that they were partially graphitized. Smaller, discrete particles of sheet-like material were also commonly seen, and these could be globular or tube-like in form [2]. The possible origin of these, and of the other contaminants described here, is discussed in the next section.

In addition to poorly graphitized carbon, platelets of crystalline graphite were commonly observed on the Agar, Taab and SPI grids. An example is shown in Fig. 1(b).

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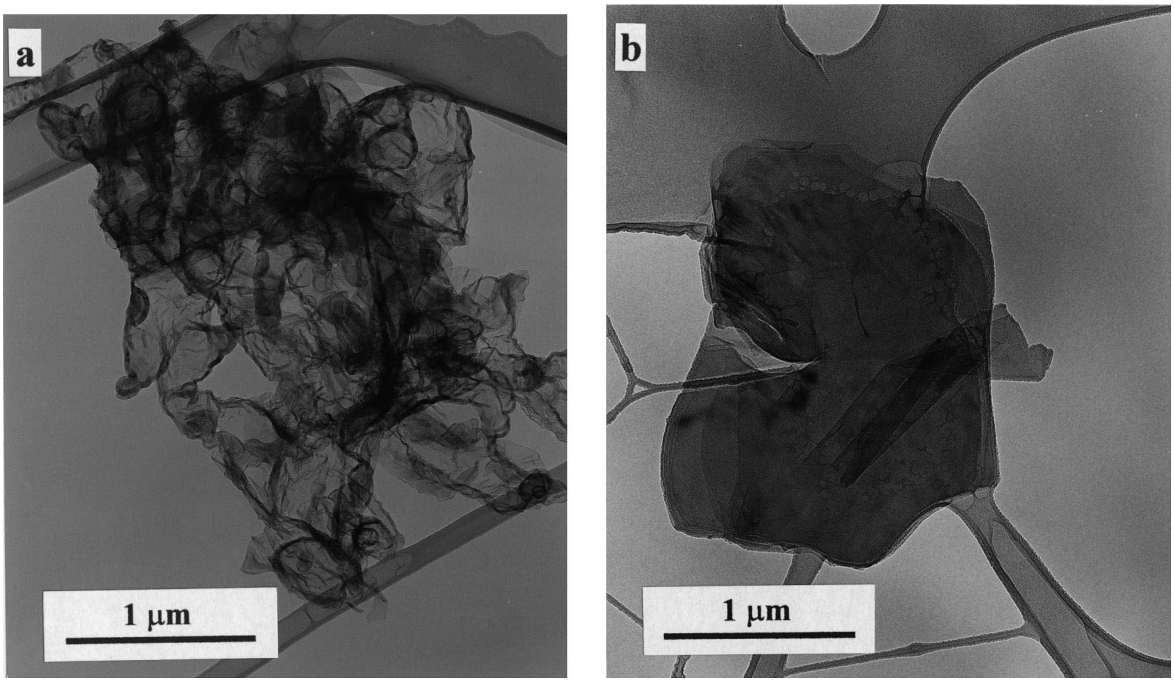

Fig. 1. Typical carbonaceous contaminants observed on commercial holey carbon support films. (a) Poorly graphitized carbon. (b) Graphite platelet.

Selected area electron diffraction confirmed that such particles were well-crystallised graphite.

Less common than the particles shown in Fig. 1, but nevertheless present on almost all of the Agar, Taab and SPI grids, were carbon nanotubes and nanoparticles. These often occurred in clusters, as shown in Fig. 2. High-resolution images showed that the tubes were invariably multi-layered, and capped at both ends, as observed in nanotubes prepared by the conventional arc-evaporation method. Fig. 3(a) is a typical high resolution image showing a tube in the cap region. Fig. 3(b) shows a number of carbon nanoparticles apparently embedded in the amorphous carbon support film.

Considering now the Oken Shoji grids, these were slightly different in appearance to the other grids, as they had a double-layer support film. This consisted of a thin plastic film coated with amorphous carbon. In the case of the Agar, Taab and SPI grids, the plastic film had been removed leaving just amorphous carbon, as discussed in the next section. The contaminants found on the Oken Shoji grids also differed slightly from those found on the others. Thus, ''crumpled sheet'' particles of the kind shown in Fig. 1(a) were not seen, but platelets of graphite, carbon nanotubes and carbon nanoparticles were commonly observed. A further kind of contaminant, not seen on the other grids, was also found on the Japanese grids. These were particles of film-like material of the kind shown in Fig. 4(a). Contaminants of this kind have been discussed

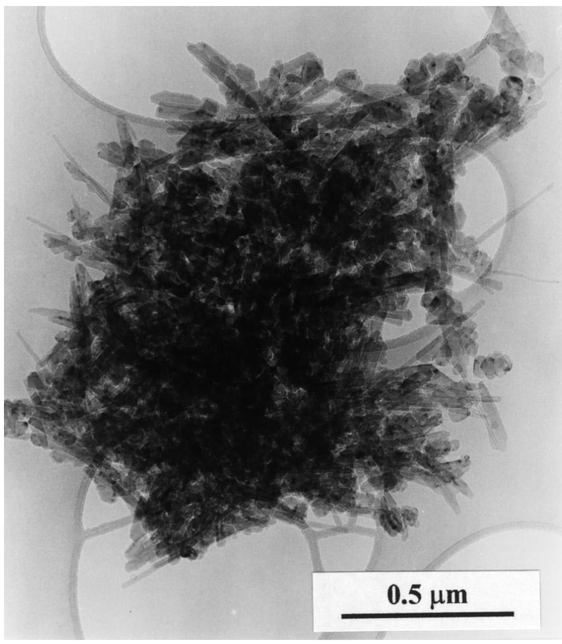

Fig. 2. Cluster of nanotubes and nanoparticles on lacey carbon support film.

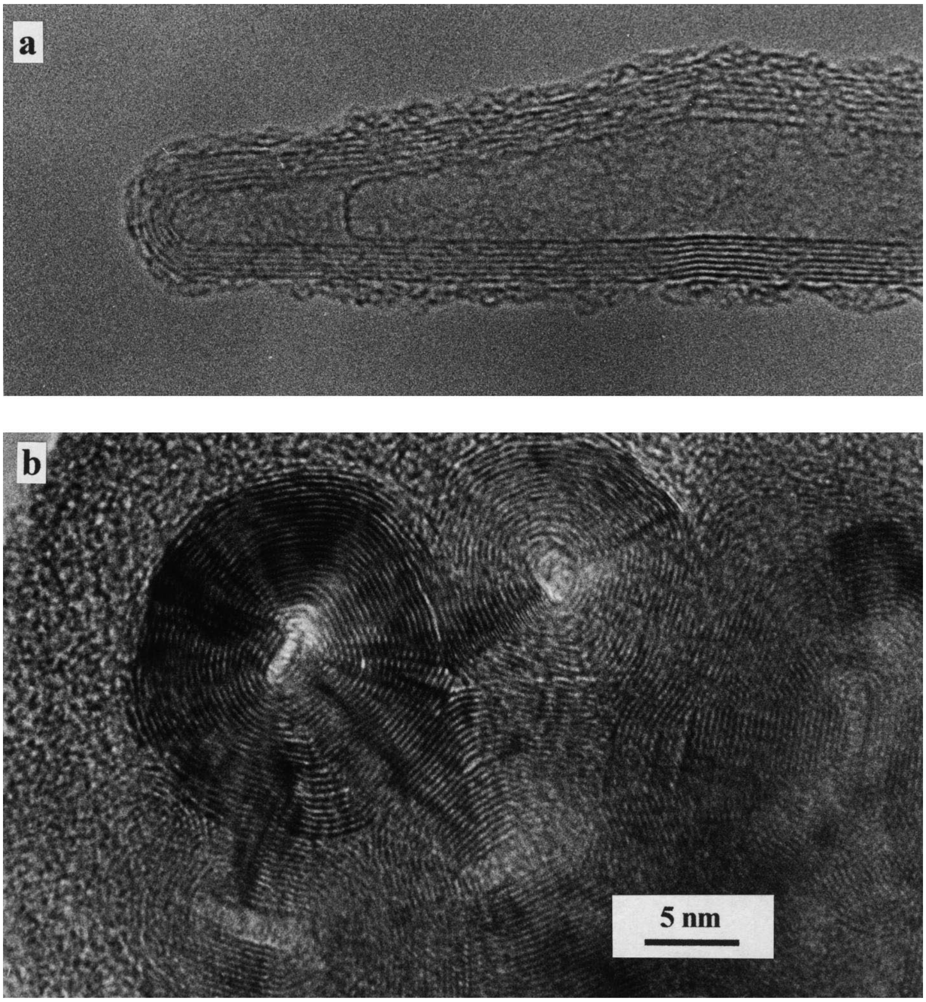

Fig. 3. (a) High resolution image showing typical carbon nanotube in the tip region. (b) Carbon nanoparticles embedded in carbon support film.

previously by Ando [3]. The particles were often approximately hexagonal in shape, and EDX microanalysis showed that they contained only carbon. However, selected area electron diffraction patterns of the particles showed that they were not graphite. A typical diffraction pattern is shown in Fig. 4(b). This has hexagonal symmetry, and the positions of the inner six spots correspond to a lattice spacing of approximately 0.46 nm. The particles were highly beam-sensitive, and lost their crystallinity after a few minutes' exposure to an electron beam. The effect of irradiation on the particles was to produce a mottled appearance, with many circular pits, as shown in Fig. 4(c).

Ando has suggested that these particles could be crystals of carbyne, i.e. *sp*-bonded carbon [3]. Certainly the electron diffraction patterns would seem to be consistent with the hexagonal carbyne structure, for which $a_0 = 0.9098$ nm and $c_0 = 1.482$ nm [4]. An alternative possibility is that the particles could be regions of the plastic film which have crystallised, although it is not known whether the polymer used in these grids (cellulose acetobutyrate) crystallises in this form.

4. Discussion

Before discussing the possible origin of the contaminants described in this paper, we need to consider the techniques used to prepare carbon support films. A typical method would be as follows [5]. Firstly, a plastic film would be formed by applying a solution of the plastic onto a glass slide or onto the surface of water. The plastics most widely used for this purpose are Formvar (polyvinyl formal) and Triafol (cellulose acetobutyrate). The thin plastic films would then be attached to metal grids. If holey

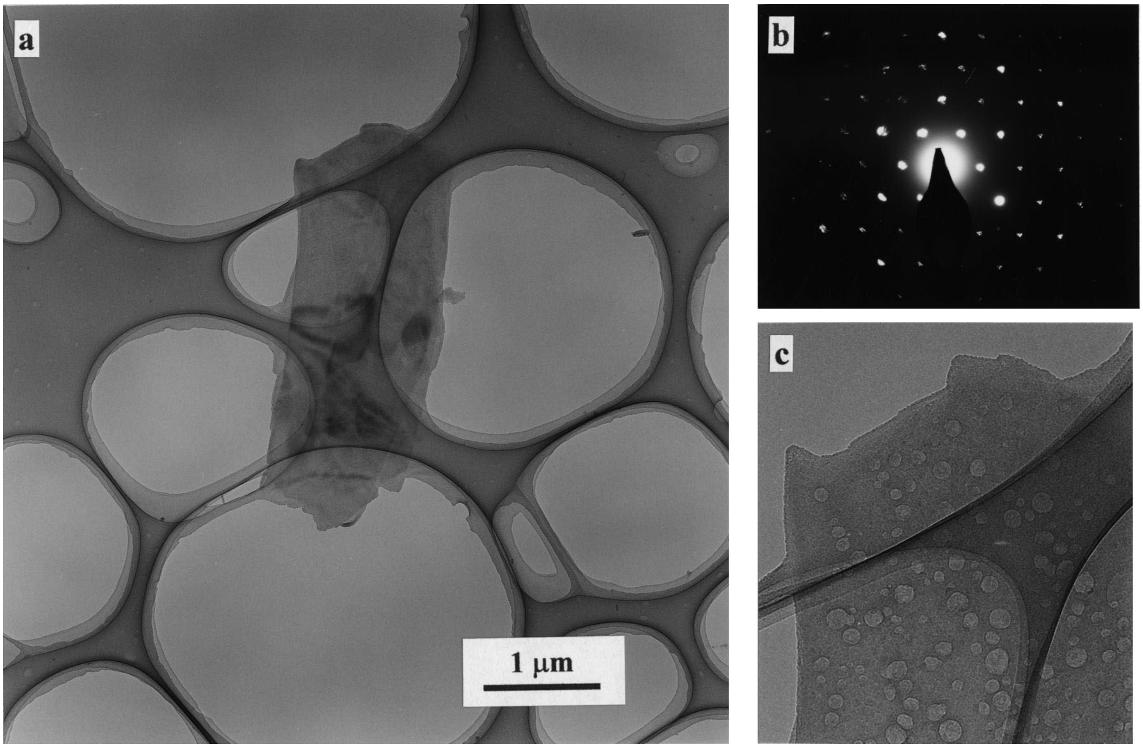

Fig. 4. (a) Possible carbyne particle found on commercial holey carbon film. (b) Selected area diffraction pattern from crystal shown in (a). (c) Same particle following irradiation with electron beam.

films are required, a fine dispersion of an immiscible liquid is added to the solution of plastic before casting. Next, the plastic film would be coated with amorphous carbon by the arc-evaporation of graphite rods. The resulting double-layer films are now usable as specimen supports, and the Oken Shoji grids examined here are of this type. However, the presence of the plastic makes the films rather thick, so it is usual to remove the plastic, either by dissolution or by heat treatment. This leaves just the amorphous carbon as a support film, as is the case with the Agar, Taab and SPI grids.

We can now attempt to explain the formation of the various types of contaminant. Poorly graphitized particles of the kind shown in Fig. 1(a) probably form as a result of partial fracturing and carbonization of the thin plastic film during dissolution or heat treatment [1,2]. This explains why they are observed on the Agar, Taab and SPI grids but not on the Oken Shoji grids. Graphite particles such as that shown in Fig. 1(b), on the other hand, are unlikely to have formed in this way since the degree of crystallinity is too high. It is likely that these are fragments of graphite which have broken away from the electrode rods during arc-evaporation.

It also seems certain that the carbon nanotubes and nanoparticles which were seen on almost all of the grids examined must also have formed during arc-evaporation. It has been known for about ten years that fullerene-related carbon structures including nanotubes can be produced by the arc-evaporation of graphite [6,7]. The only significant difference between the technique for nanotube synthesis and the method used in making carbon films for TEM is that in the former case an atmosphere of helium, rather than a vacuum, is employed in the arc-evaporation vessel.

As far as crystals of the kind shown in Fig. 4 are concerned, the origin of these is not clear. If they are genuinely crystals of carbyne they may have formed during arc-evaporation, as suggested by Ando [3]. On the other hand, the fact that they were only seen on the Oken Shoji grids, which retain the plastic film, suggests that they may be regions of crystalline polymer. Whatever their true nature, their presence could clearly be a source of confusion in TEM studies of carbyne.

The field in which the presence of carbon contaminants on TEM support films has caused most confusion is the relatively new area of carbon nanotube studies. In particular, it seems likely that a number of reports describing new methods of nanotube synthesis may be erroneous. A possible example is provided by a paper published in 1996 by Cho and colleagues, entitled ‘‘Synthesis of carbon nanotubes from bulk polymer’’ [8]. This paper described the formation of nanotubes by the heat treatment of a polymer in air at 400°C. However, when one examines the

TEM images of nanotubes shown in this paper they are very similar to the clusters found on commercial TEM grids, such as that shown in Fig. 2. There are a number of other reports of carbon nanotube synthesis in the literature which also appear to be highly dubious.

Another area where carbonaceous contaminants on TEM grids appear to have caused confusion is the study of meteoritic carbon. In 1981, Smith and Buseck reported TEM studies of carbon extracted from the Allende meteorite [9]. Among the structures they described were carbon nanoparticles with outer diameters of the order of 30–50 nm, which were very similar in appearance to those shown in Fig. 3(b). Although this paper has been quite frequently cited in the literature, and has been used to support the idea that meteorites contain fullerene-like structures [10], it seems likely that the particles observed by Smith and Buseck were actually grid contaminants. The observation by Whittaker and colleagues that carbynes are present in meteorites [11] may also be incorrect. The carbyne-like crystals shown in their paper are very similar to those found on the Japanese commercial TEM grids studied here.

Is there a solution to the problem of carbonaceous contaminants on TEM support films? One possibility might be to use plastic films with no carbon coating. Such films should contain no nanotubes and nanoparticles, but might be too unstable under an electron beam for high resolution work. Support films made from silicon monoxide are also available, but these also tend to be unstable. In the absence of suitable alternative supports, the only answer may be to proceed with care.

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