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X.Y. Song*, W. Cao and A.J. Hunt

Energy & Environment Division
Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

*Permanent address:
National Laboratory for Fine Ceramics & Structure
Shanghai Institute of Ceramics
Chinese Academy of Sciences
Shanghai, China

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AEM AND HREM EVALUATION OF CARBON NANOSTRUCTURES IN SILICA AEROGELS

X.Y. SONG*, W. CAO AND A.J. HUNT

Energy and Environment Division, Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

*Permanent address: National Lab for Fine Ceramics and Structure, Shanghai
Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China

ABSTRACT

Nanostructured carbon has been deposited in silica aerogels by chemical vapor infiltration using acetylene or ferrocene at moderate temperatures. Using analytical electron microscopy and high-resolution electron microscopy, we have observed various carbon rings and nanotubes in the silica aerogel-based carbon composite. Both X-ray microanalysis and nano-probe diffraction techniques have been used to confirm the presence of those carbon nanostructures. The morphologies and structural properties of the carbon nanotubes and rings have also been examined in detail.

INTRODUCTION

The discovery of novel carbon tubes of nanometer dimensions [1, 2] has greatly stimulated studies in the field of carbon fiber growth. Their potential applications in electronics and advanced materials have been suggested [3, 4]. Theoretical studies predict that their electronic properties depend on the diameter of the tube and degree of helicity [5, 6]. Much research has focused on the texture and formation processes of carbon nanostructures [7-11]. Up to now, the synthesis of carbon nanotubes is based on an arc discharge method similar to that of Ebbesen and Ajayan [7]. No other methods have been reported on forming carbon nanotubes. In this paper we report the observation of not only carbon nanotubes but also nanometer-scale carbon rings and carbon fibers in silica aerogels by high-resolution electron microscopy (HREM). In addition, the carbon rings were examined and evaluated *in situ* using analytical electron microscopy (AEM).

EXPERIMENTAL

Silica aerogels are highly porous materials prepared using sol-gel processing and supercritical solvent extraction [12]. The first step is to mix tetraethylorthosilicate (TEOS), water, alcohol and catalyst (usually a base e.g., ammonia) in appropriate proportions. TEOS undergoes many steps of hydrolysis and condensation reactions, leading to the formation of a soft material called an alcogel. Then liquid carbon dioxide is used to replace the fluid in the alcogel and evacuated above the supercritical temperature and pressure to make aerogels. Silica aerogels have a high porosity (90% or higher) and surface area (800-1000 m²/g), an ideal matrix for the chemical vapor infiltration of a second solid material on an extremely fine scale. The deposition of carbon was carried out in a tube furnace by the decomposition of acetylene at 550°C and post-treated in an inert atmosphere at 670°C for 0.5 h. The carbon deposition was found to distribute homogeneously throughout the aerogel

volume and the weight of the composite material increased by about 8.7% after the deposition of 1 h. In another similar experiment, carbon and iron particles were simultaneously deposited in the aerogel by the decomposition of ferrocene at 120°C for ~20 h in a helium atmosphere (~200 torr). The as-deposited samples were further treated in an inert atmosphere at 700°C for about 1 h. More detailed information on the deposition process can be found elsewhere [13]. HREM on the carbon-doped silica aerogel was performed using a JEM-200CX and TOPCON-002B operating at 200KV. The JEM-200CX analytical electron microscopy(AEM) is equipped for energy dispersive X-ray spectroscopy (EDS) with an ultra-thin window germanium detector capable of detecting elements down to C. Both X-ray microanalysis and electron nano-probe diffraction techniques were used to identify the presence of carbon nanotubes and rings in the aerogel composite. Samples for HREM studies were ground to fine powders in acetone and the suspension was dipped onto copper grids covered by a holey carbon film for transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

HREM observations show that some of the carbon in silica aerogels has an unusual morphology of graphite fibers and tubes. The length of carbon fibers ranges from several to hundreds of nm with the width varying from several to tens of graphite layers. The typical carbon nanotubes in the aerogel have a length of up to ~100 nm and a width of ~10 nm. Figure 1 is an HREM micrograph of a typical carbon nanotube

Fig. 1. HREM image showing (a) cone tip of the carbon nanotube and (b) three adjacent nanotubes parallel to each other.

surrounded by the amorphous silica. Statistically speaking, carbon nanotubes are observed under TEM on several occasions in a 1-hour period. The tubes have {002} lattice images of the graphite structure along the tube axes. The tube shown in Fig.1a consists of 12 symmetric graphite sheets with a spacing of 0.34 nm and a diameter of ~12 nm. Termination of the tube showing a cone tip is in agreement with Iijima [14] who reported that the conical surface in carbon nanotubes corresponds to the presence of five pentagons at the tip surface and that the cylindrical tubes are closed usually by polyhedral caps. Three nanotubes arranged almost parallel to each other can be identified in Fig.1b. There are a total of four tubes marked by the numbers 1 through 4, respectively; tubes 2 and 3 are overlapped perpendicularly but in parallel to tubes 1 and 4. This observation is very similar to that of R.S. Ruoff [2] who discovered two nanotubes parallel to each other. In addition, two small rings or tube derivatives can be seen in Fig. 1b.

We have also found some interesting structures as shown in Fig. 2 for a seamless graphite ring. The graphite ring has an outer diameter of about 100 nm and a wall thickness of 20 nm. In order to confirm whether it is a ring or a hollow sphere, the electron nano-probe diffraction technique (minimum probe diameter 2 to 5 nm) in ultra-micro area was used. The results of the electron nano-probe diffraction for the ring show strong (002) spots as shown in the top inset of Fig. 2. Indexing of the diffraction pattern indicates it is a graphite structure with the strongest intensity being from (002). The nano-probe diffraction corresponding to an empty area in the center of the ring (marked by E), however, exhibits the amorphous character as shown in the bottom inset of Fig. 2. This means that the image observed is indeed a ring and not a spherical shell structure. If there were any graphite structures in the center of the ring, the diffraction pattern would have contained strong diffraction spots. The electron micrograph shown in Fig. 3 is enlarged from that of Fig. 2. It can be seen clearly that the ring wall is composed of stacks of ~60 graphite layers (or sheets) with a spacing of 0.34 nm. The graphite layers winding off the ring wall (marked by D) may have been caused by grinding of the TEM sample.

Fig. 2. TEM micrograph of a circular carbon ring. The top inset is the electron nano-probe diffraction pattern for the ring wall and the bottom inset for an area in the center of the ring.

Fig. 3. HREM image enlarged from Fig.2.

Fig. 4. TEM (a) bright and (b) dark field images of an irregularly shaped carbon ring. The inset is the corresponding SAD pattern.

Fig. 5. EDS microanalyses of the ring structure shown in Fig. 4:
(a) the ring wall and (b) the ring center.

It is further necessary to confirm the composition of the rings present in the aerogel composite. The rings observed under TEM range from 30 to 500 nm in diameter. Some have an irregular shape while others appear circular much as those shown in Figs. 2 and 3. Shown in Fig. 4 are the TEM bright and dark field images of the graphite ring having an outer size up to 400 nm and a wall thickness of 40 nm. The ring has a polyhedral shape which requires total 12 pentagons to be placed into hexagonal graphite sheets [15]. The result of the select area diffraction (SAD) patterns (the inset in Fig. 4) shows the separate (002) spots and coincides with the ring morphology. We can also see that much of the ring except a small edge is suspended in midair without being supported by the holey carbon film on the copper grid. So we can get an accurate EDS spectrum for the ring.

Compositions for the wall and the center of the ring are identified in Fig. 5 (a) and (b), respectively, with the size of the probe being equal to approximately 20 nm. The ring wall has a strong carbon peak, indicating it is a graphite structure (the low Cu peak comes from copper grid). The EDS spectrum for an amorphous area near the center of the ring shows a very low carbon peak but high intensities of Si, O and Fe, which corresponds to the silica aerogel containing some iron or iron oxide decomposed from ferrocene in the deposition process.

Our electron microscopy studies have confirmed the presence of carbon nanostructures including rings and tubes in the silica aerogel-based composite. The process is different from the arc discharge method and it remains unclear how such carbon nanostructures are formed in the silica aerogel having a mean pore diameter of 10-20 nm. Further work is under way to identify and better control the processing parameters for the synthesis of carbon nanotubes and rings.

CONCLUSION

The presence of carbon nanotubes and other nanostructures in the aerogel composite has been identified by high-resolution electron microscopy. Using analytical electron microscopy and electron nano-probe diffraction technique, the morphologies of the ring structure have been further evaluated. The carbon ring has a structural feature composed of (002) graphite sheets with the ring center containing little carbon and being amorphous as expected.

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