Nanoscale Encapsulation of Molybdenum Carbide in Carbon Clusters

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Research into the formation and growth of rounded forms of carbon (concentric onion shells[1] and needle-like nanotubes[2]) from the plasma formed during graphite vaporization is at present attracting considerable interest.[3] It has been already established that some metals show catalytic activity in the formation of these nanoclusters, in certain cases leading to encapsulation of crystalline metal carbides in the intracluster void space (e.g., $SC_{15}C_{19}$,[4a] YC_2,[4b] LaC_2,[4c−e] CeC_2,[4f,g] Gd_2C_3,[4h] TiC,[4b] V_4C_3,[4i] ZrC,[4i] TaC,[4g,j] and HfC[4k]). This offers a unique opportunity to synthesize metal carbide nanocomposites and probe the properties of materials as they are constrained in nanoscale environments. In this communication we report on the synthesis and structural and magnetic characterization of carbon nanoclusters containing MoC crystals, as they form on the cathode during the dc discharge. Unlike the regular synthesis of the bulk solid that leads to the formation of the hexagonal-close-packed structural form, we find that the carbide synthesis within the nanocluster environment stabilizes a different structural form, namely, face-centered-cubic MoC. This reveals an important role for the carbon nanoclusters and/or nanotubes, as yet little explored, of catalyzing the synthesis of materials with novel structural forms in their nanoscale environment.

Samples were prepared with an arc-discharge dc generator used for routine fullerene production. Graphite rods of 6 mm diameter were used. A 1 mm diameter hole 3 cm in length was drilled in the center of the anode rod and a 3N Mo wire (Aldrich 99.9%) was inserted. The conditions employed for the arc discharge at a He pressure of 500 Torr were 20 V and 75 A dc current.

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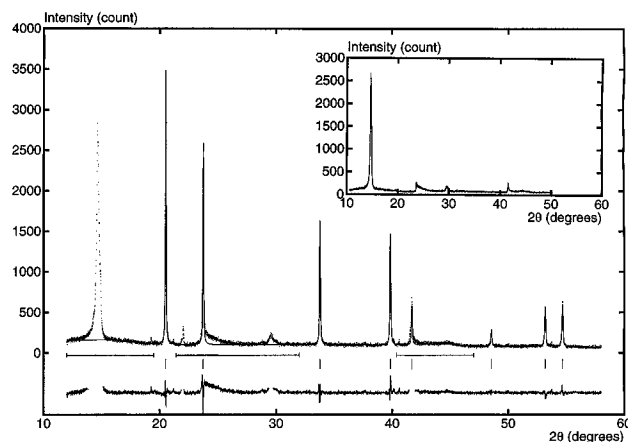
Figure 1. Observed (points) synchrotron X-ray diffraction profile of carbon nanoclusters encapsulated with molybdenum carbide ($T = 283$ K, $\lambda = 0.8725$ Å). The solid line is the calculated diffraction profile of MoC, and the lower panel shows the difference profile. The horizontal lines above the marks indicate the regions excluded in the refinement. Vertical marks indicate the observed reflections. The inset shows the diffraction profile of carbon nanoclusters without metal carbide encapsulation.
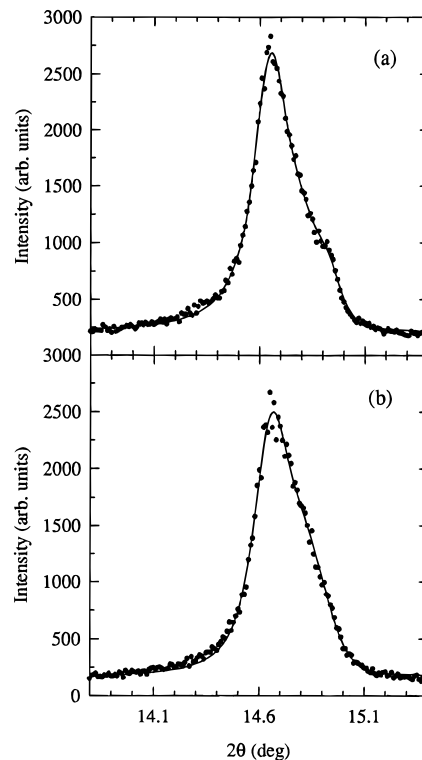

Figure 2. Expanded view of the diffraction profile of (a) MoC encapsulated nanoclusters and (b) pure carbon nanoclusters in the vicinity of the (002) reflection, showing the enhanced double peak character in (a).

The deposit which formed on the inner core of the cathode was collected by scraping and studied by HRTEM (with a JEM4000 (400kV) and a HITACHI 7100 (125 kV)), SQUID magnetometry (with a Quantum Design MPMS magnetometer), and powder X-ray diffraction (with both a Siemens D5000 diffractometer (Cu Kα radiation) and also the high-resolution diffractometer at the Station 9.1, SRS, Daresbury Laboratory ($\lambda = 0.8725$ Å, $2\theta = 12-58°$). Data analysis was performed
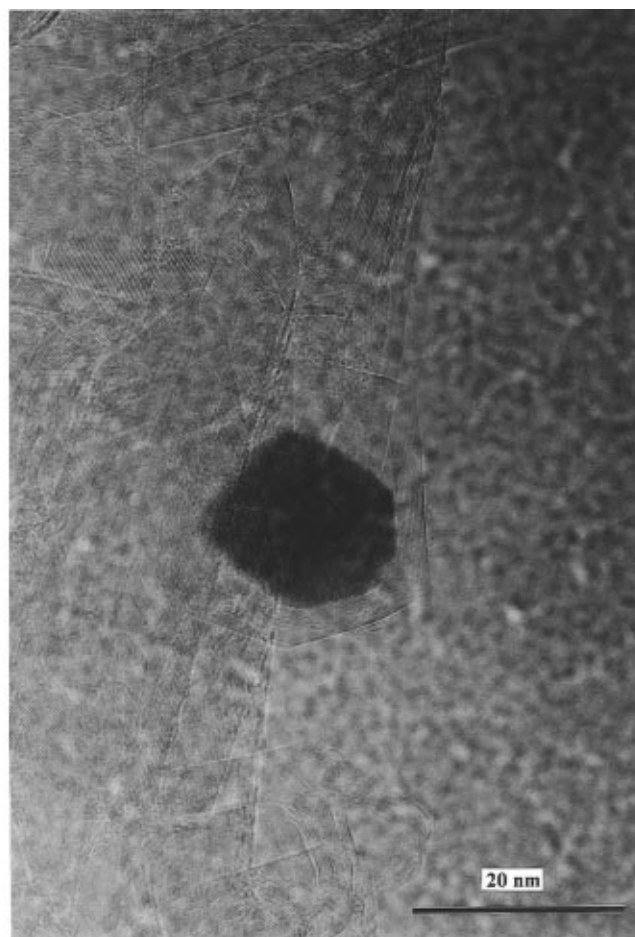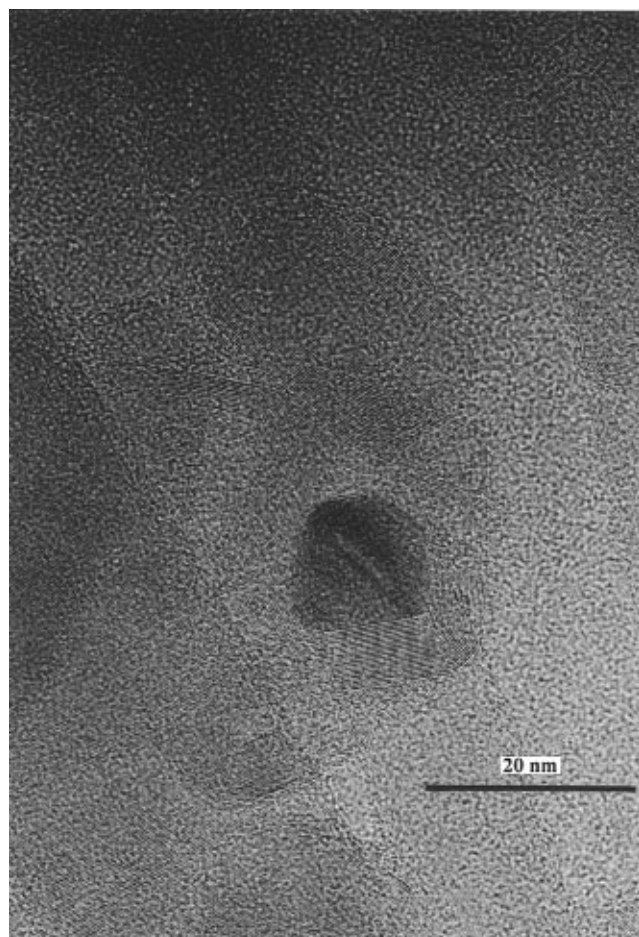
Figure 3. Representative HRTEM images of encapsulated cubic MoC crystals in carbon polyhedral particles. The images show the incomplete filling of the intraparticle void space.

Table 1. Refined Parameters for MoC (Space Group *Fm3m*) Obtained from Rietveld Refinement of Synchrotron Powder X-ray Data at 283 K[a]

atom	x/a	y/a	z/a	$B(\text{iso})/\text{Å}^2$	site occ
Mo	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.23(9)	1
C	0	0	0	2(1)	0.98(14)

[a] Estimated errors in the last digits are given in parentheses. The X-ray wavelength is 0.8725 Å. Lattice constant, $a = 4.2480(1)$ Å; R factors, $R_{wp} = 10.6\%$, $R_I = 3.0\%$, $R_{exp} = 6.0\%$.

with the PROFIL suite of Rietveld analysis programs.[5]

Figure 1 shows the synchrotron X-ray diffraction profile of the extracted cathode deposit at 283 K. As it is apparent, there are two sets of reflections present, one arising from carbon (tubes, particles) nanostructures, the other from molybdenum carbide; it is noteworthy that there is no evidence of any unreacted Mo metal. The MoC peaks index on a face-centered-cubic (rock salt type) unit cell with a lattice constant $a = 4.2480(1)$ Å. There is an accidental overlap of the (200) MoC with the (100) carbon peak and the (222) MoC with the (110) carbon peak, implying a remarkable coincidence in the lattice dimensions of the metal carbide formed and the nanostructures. Rietveld refinement of the carbide structure was performed in space group $Fm3m$ after excluding the parts of the profile contaminated by carbon nanostructure reflections. Both Mo and C atoms occupy positions in the fcc unit cell fixed by symmetry. As a result, besides the lattice constant and

peak profile parameters, only the thermal factors of the atoms were refined. Stable refinement was quickly achieved, confirming the rock salt structure of the carbide. As the lattice constant derived is smaller than that reported in the literature for fcc β-MoC ($a = 4.281$ Å)[6], an attempt was also made to refine the carbon atom occupation number. No evidence for carbon substoichiometry was revealed ($N = 0.98(14)$) for the present sample, but this result may be inaccurate, given the low X-ray scattering power of carbon and the limited angular range of the present data; N also correlates with the isotropic temperature factor, $B(\text{iso})$ which is larger than expected. The final results are collected in Table 1.

The inset in Figure 1 shows the synchrotron X-ray diffraction profile of carbon nanotube/nanoparticles, collected under the same conditions. It is evident that the diffraction pattern is little affected by the presence of the encapsulated MoC. If we focus on the (002) reflection, we find essentially identical mean interlayer spacings, $d = 3.420$ Å for the MoC encapsulated nanoclusters, $d = 3.415$ Å for the carbon nanotubes (Figure 2). This is somewhat larger than the spacing in graphite ($d = 3.35$ Å) and has been explained previously[2] by invoking the curvature of the tubules and an increased van der Waals interaction between the layers. Closer inspection of the (002) reflection in both materials (Figure 2) reveals a pronounced shoulder on the high

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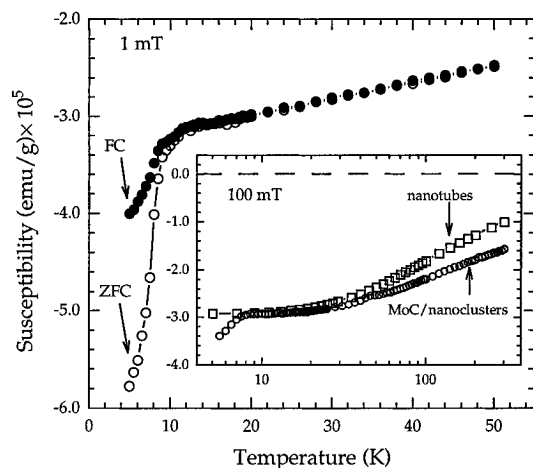
Figure 4. Magnetic susceptibility as a function of temperature for MoC encapsulated carbon nanoclusters, measured with a SQUID magnetometer both under ZFC ($\bigcirc$) and FC ($\bullet$) conditions in a field of 1 mT. The inset shows ZFC data (100 mT) up to a temperature of 300 K for a second sample together with data on pure nanotubes ($\square$).

angle side, corresponding to an identical interlayer spacing of $d = 3.362$ Å in both cases and implying the presence of material with graphitic dimensions, ca. 8−9%.

HRTEM images reveal the presence of an abundance of cubic MoC crystals (typical dimensions ∼10−15 nm) encapsulated almost exclusively in polyhedral carbon particles (Figure 3). The images also show that the void space in the nanoparticles is not usually filled completely. The observed behavior contrasts with the case of TaC which is present in both nanoparticles and nanotubes and appears to grow epitaxially, with its layer fringes parallel to the walls of the tubes.[4g,j] Such differences may be traced to the melting points of the carbides (2200 °C for MoC, 3985 °C for TaC) that straddle the sublimation temperature of carbon (2500−3500 °C at low pressures). While TaC crystallizes first and the carbon atoms start to condense around it, leading to encapsulated nanotubes and nanoparticles, the opposite in general would be expected to occur for MoC which crystallizes at a much lower temperature, e.g., after the condensation of carbon has occurred, leading to inefficient incorporation inside nanoparticles.

In Figure 4, we show the results of the susceptibility measurements over the temperature range 5−50 K. Data were collected both after zero-field cooling (ZFC) and field cooling (FC) in a field of 1 mT. A diamagnetic transition with an onset at ∼10.5 K is clearly evident. This indicates a transition to a superconducting state

and is ascribed to the encapsulated MoC, consistent with the superconducting properties exhibited by all members of the molybdenum carbide family.[7] These show relatively high T_c's (up to 14.3 K) regardless of symmetry, composition, and electron concentration, presumably associated with the common Mo_6C octahedra present in all of them. The FC curve in Figure 3 reflects the Meissner effect and shows a sizeable expulsion of the magnetic field. However, the somewhat large difference between the ZFC (flux exclusion) and the FC curves in Figure 3 indicates fairly strong pinning of the magnetic vortices in this material. The multiphase nature of the present samples precludes a quantitative characterisation of the superconducting state. The inset of Figure 3 shows the measured susceptibility of a second sample at 100 mT (under ZFC conditions) up to 300 K together with a measurement on carbon nanoclusters. The diamagnetic response arises from the carbon nanocluster material and is consistent with results reported earlier.[8] It is noteworthy that the measured susceptibility of the nanotubes is much larger than in the case of any other form of carbon.

In conclusion, we find that MoC encapsulated carbon nanoparticles are produced when graphite rods, containing a Mo core, are exposed to an arc discharge. Lack of nanotube encapsulation may be attributed to the low mp of the carbide. Remarkably encapsulation stabilises the face-centered-cubic form of MoC with a somewhat contracted lattice spacing, compared to the known dimensions of the bulk material, at the expense of the commonly encountered hexagonal-close-packed form. The encapsulated fcc MoC is superconducting with an onset transition temperature ∼10.5 K.

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