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Nanometer sized CeC_2 crystals encapsulated within gigantic super fullerenes

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Nanometer-sized crystals encapsulated within gigantic super fullerenes are synthesized by d.c. arc evaporation of composite carbon rods containing ~3 wt.% CeO_2. Elemental analysis shows that Ce and C are the only elements present in significant quantities in the encapsulated crystals. Referring to the phase diagram for the Ce-C system, electron diffraction measurements give an unambiguous identification of the encapsulated crystals. Lattice constants of the encapsulated crystals are in excellent agreement with those of CeC_2 within 1.6% accuracy.

1. INTRODUCTION

Recently, one of the authors(YY) reported a synthesis of CeC_2 crystals encapsulated within gigantic super fullerenes(GSFs): the carbon cages with a few tens of nanometer sizes and with shell structure. In that work an identification of the encapsulated crystals was made based on the lattice fringe images observed by transmission electron microscope (TEM) referring to the phase diagram for the Ce-C system. This work is an extension of the previous one; efforts have been made in elemental analysis and in electron diffraction measurements.

2. SAMPLE PREPARATIONS

To produce encapsulated crystals ceria powder, CeO_2(99.99% purity), and graphite cement(Aremco Products, 551-R) with a weight ratio of ~0.3 was mixed and then compressed into the core of carbon tube(99.999% purity; 3mm i.d. and 6mm o.d.; 8mm in length). After curing the cement at 120°C for 3h the resulting rods were baked at 400°C for 70h in vacuum(10^{-5}torr). Re-baking was done at 1400°C for 1 h in a reaction vessel(10^{-3} torr) before evaporation. The re-baking corresponds to the known carburizing reaction, and its rate is expected to controll yield of final encapsulated crystals; a successive re-baking at 2000°C for a few minutes gives that ~80% of GSFs contain the crystal, which is compared with ~50% of them at 1400 °C for 1h. The rods were used as positive electrodes, which were consumed in d.c. arc discharge and then yielded carbonaceous deposit onto a carbon negative electrode. The power of the arc discharge was 40V at 30A under partial helium atmosphere(600 torr). At the conditions, the yield of carbonaceous deposit was ~60% of the consumed rod. To remove residual CeO_2 outside the GSFs

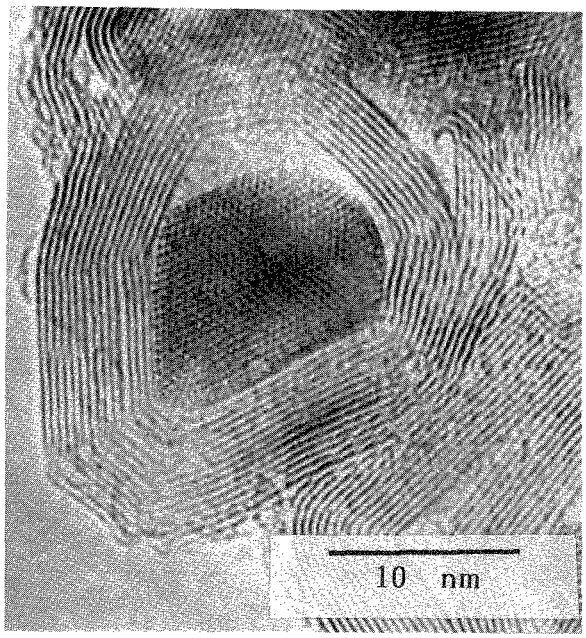

Figure 1. Bright field TEM image of an encapsulated CeC_2 crystal.

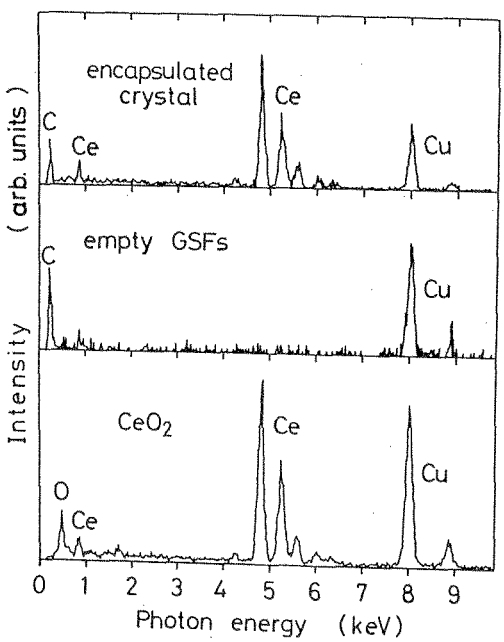

Figure 2. Energy dispersive spectra of an encapsulated crystal, empty GSFs and CeO_2.

assuming its existence, a mixture of black deposite(50mg) and sulfric acid(96% purity; 10cc) was heated at 180°C for 70h. The resulting material was washed out with distilled water. Samples dispersed into the water were collected using a centrifuge.

3. ELEMENTAL ANALYSIS

Microscopic observations were conducted for the samples using a field emission type TEM at an energy of 200 keV. Encapsulation of crystals was found for polyhedral shaped super fullerenes as shown in Fig. 1 or tubular shaped super fullerenes[2] with short length. The encapsulated crystals were 20x20x20 nm^3 in maximum dimension and occupied 50~98% of the empty space of the innermost cage. Elemental analysis for the encapsulated crystals was performed with KEVEX delta class energy dispersive spectroscopy(EDS) analyzer. The image ranges were as small as 50 nm in diameter. TEM images were recorded only from the areas that projected over holes(~50 nm in diameter) in micro-grid support film. Figure 2 shows typical EDS spectra for an encapsulated crystal, empty GSFs and CeO_2, respectively. The peaks designated Cu are due to sample holder. These spectra show that Ce and C are the only elements present in significant quantities in the encapsulated crystals.

4. MATERIAL IDENTIFICATION

Elemental analysis gives five possibilities of identification for the encapsulated crystals: face-centered cubic(fcc) phase Ce with the lattice constant of a_o= 5.1612Å; quenched body-centered cubic(bcc) with a_o=4.12Å; fcc(NaCl type) CeC with a_o=5.135Å;

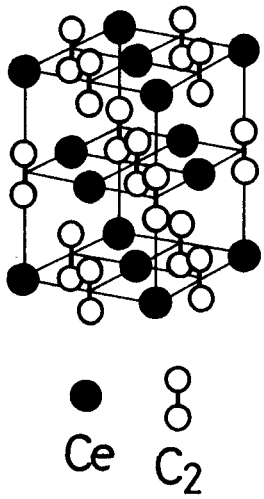

Figure 3. The crystal structure of CeC_2.

tetragonal (CaC_2 type) CeC_2 with a=3.878Å and c=6.488Å; and bcc(plutonium sesquicarbide type) with a_o=8.4476Å. These known lattice parameters permit the unambiguous identification of the encapsulated crystals.

Electron diffraction measurements showed four different interplanar spacings d. These were 3.323± 0.002Å, 3.239±0.004Å, 2.728±0.002Å and 2.083±0.002Å, and were in excellent agreement with d_{101}, d_{002}, d_{110} and d_{112}, respectively, for CeC_2 within 1.6% accuracy. Thus, we found the lattice constants of the encapsulated crystals: a=3.879±0.002Å and c= 6.478±0.052Å. The other possible identifications have been tried, but the results were, however, far from the observations within the experimental accuracy.

The crystal structure of the CeC_2 has been described as tetragonally distorted NaCl type packing of the Ce atoms and the C_2 molecules as shown in Fig. 3, where the Ce atoms are at (000) and (1/2,1/2,1/2), and the carbon atoms occupy (0,0,±z) and (1/2, 1/2,1/2±z). The carbon z-parameter is 0.4011±0.005[3]. CeC_2 is a novel material possessing metallic properties. Encapsulated CeC_2 crystals were extremely stable in air, water, and hot concentrated sulfric acid for seven months they were treated, in strong contrast to pristine CeC_2 being unstable in these conditions. This is enough evidence to prove the perfect encapsulation of the crystals.

5. CONCLUSION

Energy dispersive spectroscopy and electron microscopy gave the unambiguous identification for the encapsulated crystals which were synthesized by dc arc evaporation of composite carbon rods containing ~3wt.% CeO_2: CeC_2 with the CaC_2 type structure. The highest yield of the encapsulated crystals was ~80% of the observed GSFs.

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