Synthesis and Characterization of Calcium Endohedral Fullerenes

Cao Baopeng, Shi Zujin, Zhou Xihuang, Gu Zhennan,* Xiao Hongzhan,† and Wang Jingzun†
Department of Chemistry, Peking University, Beijing, 100871, P. R. China
†Beijing Institute of Microchemistry, Beijing, 100091, P. R. China

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The calcium endohedral fullerenes were synthesized by vaporizing the graphite anode filled with CaC_2 grains with DC arc, extracted by CS_2, and characterized by field desorption mass spectra. It is found that in the extract most fullerenes between C_{58} and C_{100} encapsulated one calcium atom and some trapped two calcium atoms inside. The results show that filling the graphite anode with CaC_2 grains is more favorable to the formation of calcium endohedral fullerenes than filling with other materials.

In recent years endohedral metallofullerenes have greatly attracted chemical researchers since they could give rise to new species or materials with novel structures and properties.[1] Up to now most of the endohedral metallofullerenes reported were prepared by vaporizing the composite graphite rods filled with metal oxides with arc burning or laser ablation method. In these methods the metal oxides filled must be reduced and carbonized before being vaporized, namely the oxygen must be removed first, otherwise the endohedral metallofullerenes can not be formed.[2] This shows that the metal carbide plays an important role in forming endohedral metallofullerenes.

The calcium endohedral fullerenes were always synthesized by vaporizing the graphite anode filled with a mixture of calcium oxides[3-7] or calcium[8] and graphite with DC arc burning method. They were also prepared by vaporizing the coorongites with laser ablation method.[9,10] Most of the doping materials contain oxides. In the preparation process, if the oxygen is not removed thoroughly, it will not only affect the formation of endohedral fullerenes but also disturb the assignment of calcium endohedral fullerenes because the oxygen can combine with fullerenes to form fullerene oxides and the molecular weight of the C_2+0 group is equal to that of calcium. Taking the above two points into consideration we used calcium carbide grains to fill the graphite anode to produce calcium endohedral fullerenes. Experiments showed that besides the $Ca@C_{2n}$ reported in literature[3-10] the extract contained many new endohedral fullerenes, such as $Ca_2@C_{2n}$ (2n = 58, 60, 62, 66, 68, 72, 78, 96).

Using a graphite anode (Φ 6 mm) with a hole (Φ 4 $\times$ 120 mm) stuffed by calcium carbide grains, the calcium endohedral fullerenes were synthesized by 100 A DC arc at a He pressure of 1.7×10^4 Pa. The soot was collected and extracted by CS_2 under the protection of Ar atmosphere. The extract was characterized by field desorption mass spectra (FDMS) with Finnigan MAT90 Mass Spectrometer.

Part of the FDMS is given in Figure 1(a, b, c, d, and e). The results show that besides the endohedral fullerenes reported in literature,[3-10] such as $Ca@C_{2n}$(2n = 60, 70, 72, 74, 78, 82, 84), in the extract there are many new endohedral fullerenes. Most of the fullerenes ranging from C_{58} to C_{100} encapsulated one calcium atom while some others trapped two atoms, such as $Ca_2@C_{58}$, $Ca_2@C_{60}$, $Ca_2@C_{62}$, $Ca_2@C_{66}$, $Ca_2@C_{68}$, $Ca_2@C_{72}$, $Ca_2@C_{78}$, $Ca_2@C_{96}$. Although two or more lanthanide atoms have been reported to be trapped into fullerenes,[2] it is novel for us to find

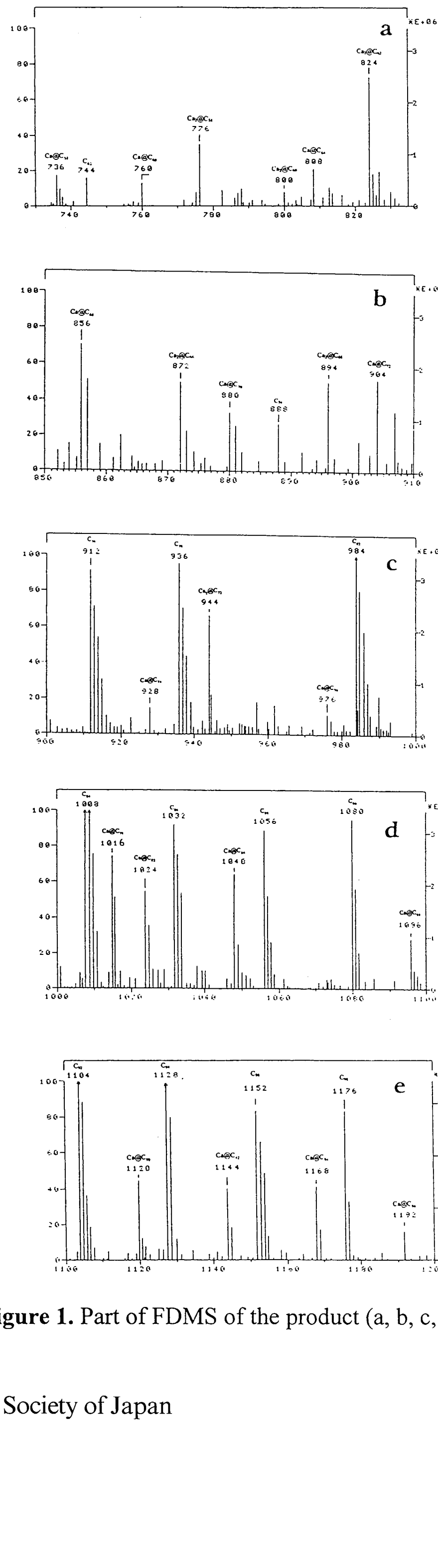

Figure 1. Part of FDMS of the product (a, b, c, d, and e).

that two calcium atoms have been encapsulated into fullerenes.

As the solubility of C_{60} and C_{70} are much higher than those of large molecular fullerenes and endohedral metallofullerenes, the endohedral fullerenes obtained were concentrated through partially dissolving the solid residue in toluene for several times. The FDMS of the products after enrichment is shown in Figure 2(a, b).

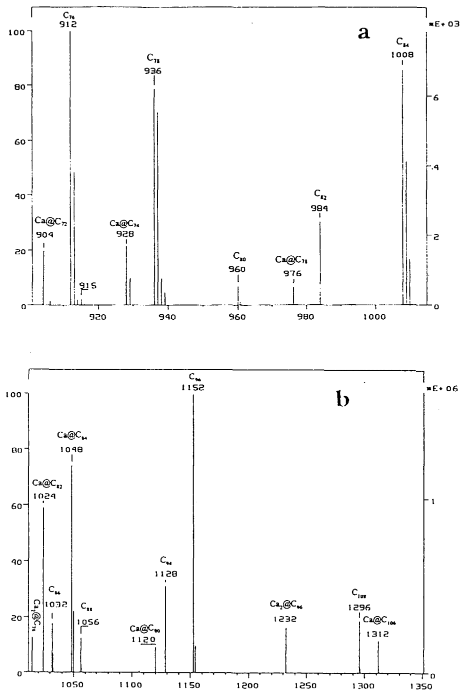

Figure 2. Part of the FDMS of the product after enrichment (a, b).

From Figure 2 it is easy to find that after removing most of the smaller fullerenes part of the endohedral metallofullerenes were lost, but some others, such as $Ca@C_{2n}$ (2n = 72, 74, 78, 82, 84, 106) and $Ca_2@C_{2n}$ (2n = 78, 96), still remained. Among these compounds $Ca@C_{82}$ and $Ca@C_{84}$ were the most abundant ones, followed with $Ca@C_{72}$, $Ca@C_{74}$ and $Ca@C_{78}$. These results indicate that the most stable calcium endohedral fullerenes are $Ca@C_{82}$ and $Ca@C_{84}$ and next to them are $Ca@C_{72}$, $Ca@C_{74}$, $Ca@C_{78}$. This stability sequence is consistent with the report[8] and that of the endohedral fullerenes of IIIB group metals.[2]

Using composite graphite rod filled with CaC_2 grains as anode to synthesize calcium endohedral fullerenes has three merits. First, it avoids the interference of oxygen during their synthesis and MS characterization, making the assignment of calcium endohedral fullerenes more accurate and reliable. Second, the species of endohedral fullerenes formed in this way are very plentiful. Besides those reported in the literature,[3-10] many new species of calcium endohedral fullerenes have been obtained. Third, this method is more favorable to the formation of calcium endohedral fullerenes than the others. Considering the formation mechanism of fullerenes and the electronic structures of calcium endohedral fullerenes and CaC_2, this can be easily understood. According to the formation and decomposition mechanism of fullerenes, C_2 group plays an important role in the formation process of fullerenes. Theoretical study shows that in $Ca@C_{2n}$ Ca atom transfers two electrons to C_{2n} to form $Ca^{2+}@(C_{2n})^{2-}$ electronic structure.[4] CaC_2, the ionic carbide with Ca^{2+} and C_2^{2-} (joined) together, can satisfy these criteria simultaneously. So it is understandable that the presence of CaC_2 is favorable to the formation of calcium endohedral fullerenes. This may be one of the reasons why the species of endohedral fullerenes prepared in this way are so plentiful. From this viewpoint we also can see why carbonizing is necessary in synthesizing endohedral metallofullerenes with the metal oxides filled.

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