Synthesis of Silicon-containing Fullerenes

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Macroscopic quantities of silicon-containing fullerenes have been synthesized by vaporizing a SiC-doped anode with DC arc discharge technique, extracted by CS_2, and characterized by field desorption mass spectra (FDMS). Besides silicon-cage-doped fullerenes, in the extract some others which are supposed to be silicon endohedral fullerenes are also found.

After the discovery of fullerenes chemists proposed that fullerenes can encapsulate atoms[1] and can be doped on cage with other elements to form materials with novel properties and uses.[2] Many metallic atoms and inert gases have been trapped into fullerene cages,[3,4] and other atoms such as N,[5-7] B,[8-11] have formed cage-doped fullerenes. There are some neutral molecules, such as CN[12] and CO[13] supposed to be trapped inside the cage. Due to the similarity to carbon, silicon atoms can replace those of carbon on fullerene cage as predicted theoretically by Siliaghi-Dumitrescu.[2] Some small silicon-carbon clusters, in which the total number of atoms is less than 10, have been experimentally studied.[14,15] Recently microscopic quantities of small silicon-doped cluster cations, such as C_nSi^+(n = 3 - 69) have been detected by laser-vaporization beam TOF-MS technique.[10,16] Due to the semiconductivity and larger radius of silicon, the silicon-containing fullerenes will have some special electronic structures and properties. Here we report the macroscopic preparation of large silicon-containing fullerenes. Besides silicon-cage-doped fullerenes, in the extract we also find some others which are supposed to be silicon endohedral fullerenes.

An anode (Φ 8mm) was filled with a mixture of SiC and graphite cement (Φ 5×120mm). The final atomic ratio of Si/C in the anode was 1:40. Before vaporization, the anode was heated to expel moisture completely under vacuum. With a pure graphite rod as cathode, the SiC-doped anode was vaporized by 100A DC arc in 2.7×10^4 Pa He atmosphere. The soot was collected under nitrogen and extracted by CS_2 at room temperature under argon atmosphere. The extract was characterized by FDMS (Finnigan MAT90 Mass Spectrometer).

From the FDMS of the extract we found some new peaks which were never present in the FDMS of the fullerenes prepared by a pure graphite rod. They should arise from SiC-doped graphite anode. We scaled up the soot preparation, recrystallized the extract in toluene, and removed off most of C_{60} and higher fullerenes. All these operations were performed under the protection of argon. The FDMS of the extract after recrystallization was shown in Figure 1. From Figure 1 it can be seen that besides those peaks from carbon fullerenes some new peaks did appear. It was found that these new peaks could only be ascribed to silicon-containing fullerenes. The new peaks and their assignments were listed in Figure 1.

From Figure 1 we can see that five kinds of compositions of silicon-containing fullerenes, such as $C_{2n-1}Si$ (2n = 60, 62,

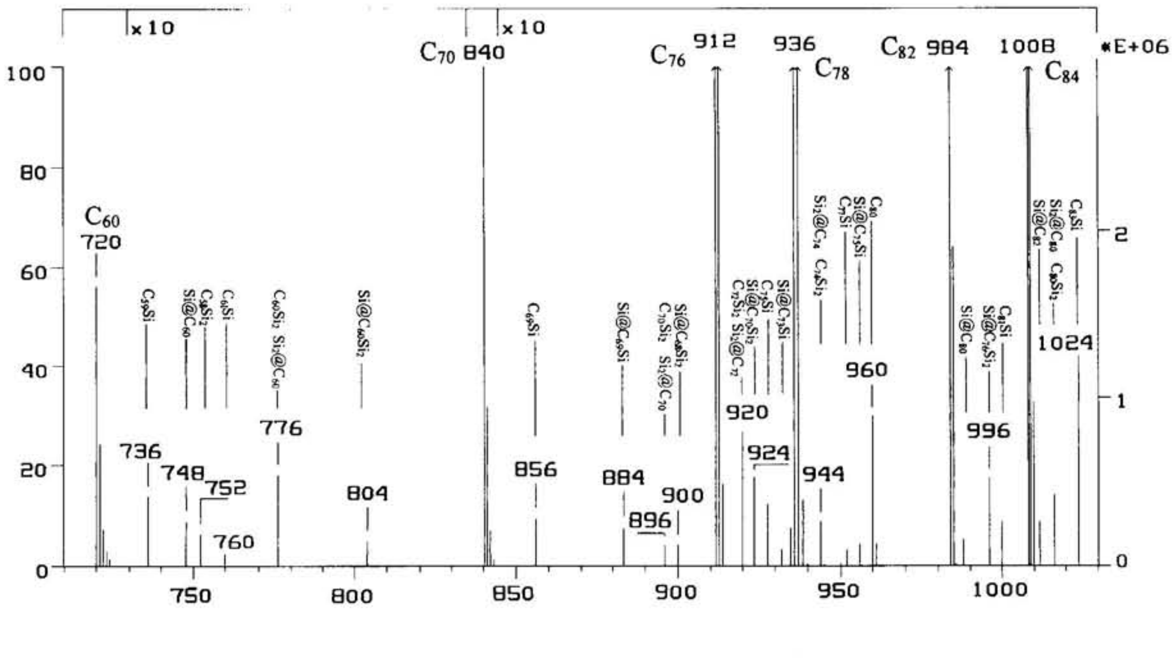

Figure 1. The FDMS of the soot extract after recrystallization.

70, 76, 78, 82, 84), $C_{2n}Si$ (2n = 60, 80, 82), $C_{2n-1}Si_2$ (2n = 70, 74, 76), $C_{2n}Si_2$ (2n = 58, 60, 70, 72, 74, 80) and $C_{2n}Si_3$ (2n = 60, 68, 70, 76) appeared. Based on the following facts, i.e., (1) the number of atoms on fullerene cage should be even; (2) the endohedral fullerenes so far known in literature usually encapsulate one or two atoms and in exceptional cases three atoms;[3] (3) the noble gas atoms[4] and even neutral molecules such as CN[12] and CO[13] are reported to be trapped in to the cages; and (4) silicon is similar to carbon, the structures of these silicon-containing fullerenes can be proposed. $C_{2n-1}Si$, in which the number of carbon atoms is odd and that of silicon is one, must be silicon-cage-doped fullerenes. This is consistent with the proposals of Shinohara[10] and Jarrold.[16] $C_{2n}Si$, with even number of carbon atoms and one silicon atom, may have two possibilities, silicon endohedral or silicon exohedral fullerenes. We think that their most probable structures are endohedral. There is supposition that in $C_{2n}Si$ the silicon atom is exohedrally linked to the cage.[10,16] In $C_{2n-1}Si_2$ one silicon atom must be on cage and the other is supposed to be trapped into the silicon-doped-cage. To $C_{2n}Si_2$, because of the similarity between silicon and carbon, the most probable structure is closed cage with the two silicon atoms cage-doped. There exists another possibility that two silicon atoms are encapsulated into the fullerene cage, specially to those with large C_{2n}. For $C_{2n}Si_3$ the structures must be more complicated. The exact structural characters of the silicon-containing fullerenes need to be further explored after being isolated and purified.

It is interesting to mention that in our work all the stable carbon fullerenes, such as C_{60}, C_{70}, C_{76}, C_{78}, C_{82}, C_{84}, etc., have been doped on cage by one or two silicon atoms. This result shows the fact that silicon is similar to carbon. However, as silicon has larger atomic radius than carbon and exhibits semiconductivity, the silicon's doping on cage might change the cage's electronic structure and properties. These changes maybe lead to interesting functional materials.

It is novel that the fullerenes, especially the silicon cage-doped fullerenes, can encapsulate silicon atom into cages. Up to now most elements trapped into fullerene cages are metals or inert gases. Nonmetallic atoms have never been reported to be enclosed into the cages. Because silicon is neither as active as metal nor as inert as noble gas, silicon endohedral fullerenes must be different from those of metals or inert gases in electronic structures and properties and worthy to be studied.

The following points can be concluded. Macroscopic quantities of silicon-containing fullerenes can be prepared by burning the SiC-doped anode with DC arc and extracted by CS_2. Silicon atoms can replace those of carbon on cages.

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