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# High Efficient Extraction of $M@C_{2n}$ (M = La, Ce ) by a High Pressure and High Temperature Method

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## Abstract

A high pressure and high temperature method was used to efficiently extract on a large scale metallofullerenes $M@C_{2n}$ (M=La,Ce) in a closed vessel under argon gas protection. With pyridine as the HPHT solvent, about 60-80% $M@C_{2n}$ and 30-55% $M@C_{82}$ can be enriched, $M@C_{82}$ is dissolved selectively; With toluene as the HPHT solvent, $M@C_{2n}$ can also be efficiently extracted, especially $M@C_{74}$, which is a new member of $M@C_{2n}$ soluble species. © 1998 Elsevier Science Ltd. All rights reserved.

*Keywords:* Metallofullerenes, High temperature and high pressure, Extraction, Pyridine.

## Introduction

Since techniques to encapsulate metals inside fullerenes in bulk by laser or arc vaporization of graphite-metal composites were developed[1], endohedral metallofullerenes have attracted special attention due to their unique structures, properties and potential application[2,3].A number of metallofullerenes include La,Y,Sc, and most of lanthnide elements have been prepared and characterized by many researchers[1-7]. More recently, important progress toward purification have been reported[3,8-11]. However, the quantity of metallofullerenes in pure form such as $M@C_{82}$ are so limited that most of physical and chemical properties are still unknown. The reasons for this are the difficulty both in the isolation techniques and

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extracting sufficient quantities of metallofullerenes from the soot due to their poor solubility in organic solvents. Furthermore, for the similar structures of fullerene family, the metallofullerenes mixed with hollow fullerenes are dissolved in solvent simutaneously. The questions of extraction are not only so much one of solubility but also the preliminary separation of metallofullerenes from the hollow ones.

Soxhlet extraction is the traditional method[2,3]. It has been found that $M@C_{82}$, the main soluble species, is soluble in some solvents, including toluene, carbon disulfide, pyridine and N,N-dimethylformamide(DMF)[1,4,10,11,13,14]. In additional, $M@C_{76}$, $M_2@C_{80}$ and $M@C_{60}$ are also soluble species[7,15-17]. Recently, a " bomb" extraction by using toluene as solvent has been reported. 20% $La@C_{2n}$ and 18% $La@C_{82}$ along with giant hollow fullerenes could be extracted[18]. However, the quantity is still small ( extractable species are 0.3% of the raw soot and the extractor volume is only 0.64 ml ) and researchers are warned to take safety precaution. Therefore, in this paper, we studied a more efficient method to extract metallofullerenes on a large scale.

## Experimental Section

Soot, containing metallofullerenes $M@C_{2n}$($M$ = La, Ce ), was generated by arcing a metal oxide impregnated graphite rod at a pressure of 13.3 kPa helium gas using the usual arc vaporization method[1,19]. In brief, the graphite rods (anodes) were drilled and filled with a mixture of metal oxide and graphite powders. The atomic ratio of metal to carbon for the resulting rods was approximately 0.01. Prior to arc burning, they were treated in two ways: (a)The synthesis chamber was pumped to 2.5 Pa and the anode was connected with the graphite cathode with a current of 200 A passed for 20 minutes. The process is called as activation *in situ* process. (b)The starting composite rod was subjected to a heat treatment at 300 °C for 2 h and carbonized at high temperature of 2000 °C for 8 h under the protection of argon gas instead of activation *in situ*. During the arc vaporization, a carbonaceous deposit was simultaneously produced on the top of cathode. After the anode was exhausted, the deposit was also used as the anode by reversing the arc polarity. This process is called as arc-back burning.

Soot generated was collected and soaked into toluene for several hours at room temperature, the insoluble part of soot was filtered and further refluxed with toluene for 24 h in a Soxhlet extractor so as to remove as much of the readily soluble hollow fullerenes as possible. Filtered again, then the precipitate was extracted with solvents in a closed vessel under the protection of argon gas at the conditions of high pressure-high temperature ( HPHT, about 100 atm, 220 °C ) for 5 h. Toluene and pyridine were studied as solvents respectively. The 50ml vessel was made from alloy steel. It is easy to extract at least 5 g precipitate each time. So by using such a vessel, extraction can be done on a large scale. The pressure in the vessel was approximately 100 atm according to temperature ( 220 °C ) and the solvents. Filtered and washed, the soluble toluene or pyridine extract containing M@$C_{2n}$ was prepared.

The samples were characterized by using desorption electron impact mass spectrometry (DEIMS) with a VG-Quattro quadruple spectrometer. The temperature of supply was 200 °C and the electron energy was 70 eV.

## Results and Discussion

Soot containing La@$C_{2n}$ was firstly produced by treatment (a) including activation combined with arc-back burning. From the analysis of the toluene Soxhlet extract of soot prior to HPHT extraction by DEIMS, the soluble portion was found to contain mostly $C_{60}$,$C_{70}$ and high empty fullerenes with a trace amount of lanthanofullerenes La@$C_{82}$. This result indicates that La@$C_{2n}$ is difficult to extract from soot by the usual method with toluene. The polarity of lanthanofullerenes is bigger than that of $C_{60}$,$C_{70}$ and similar to that of giant hollow fullerenes which probably leads to La@$C_{2n}$ being wrapped or absorbed at the surface of soot. However, It is also shown that toluene Soxhlet extraction is a convenient way to separate metallofullerens from hollow fullerenes crudely. The precipitate ( about 95% of the raw soot ) which contained mostly lanthanofullerenes needed further extracting.

On the study of solubility of giant fullerenes in o-xylene, R.S.Ruoff et al extracted a quantity of giant fullerenes by using high pressure -high temperature method (30 atm, 300 °C )[20]. Therefore, the extraction of metallofullerenes was tried under HPHT conditions. In order to avoid chemical the reaction, the whole procedure was protected under argon gas. Fig1 shows the DEIMS of HPHT toluene extract(0.5% of the precipitate). Besides the hollow fullerenes ($C_{60}$,$C_{70}$,$C_{74}$,$C_{76}$,$C_{78}$,$C_{80}$), there are other kinds of peaks due to lanthanofullerenes La@$C_{2n}$ (2n=82,80, 78,76,74 ) as almost abundant as the giant fullerenes, The peak for La@$C_{82}$

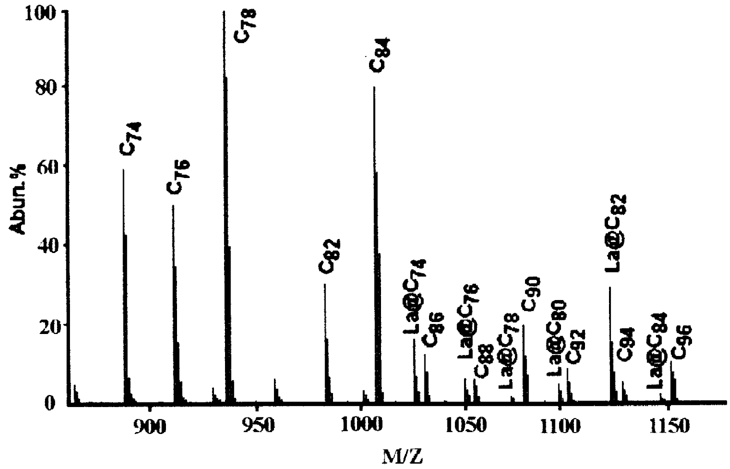

Fig.1, The DEIMS of high temperature -high pressure toluene extract of La-containing soot produced by arc back-burning with activated anode in situ(treatment (a)).

is the most intense and that for La@$C_{74}$ is the second among the La@$C_{2n}$. It is noted that in the previous study, regardless of the laser desorption mass spectrometry or the negative ion/desorption chemical ionization of the raw soot, the intensity of La@$C_{74}$ is the strongest among La@$C_{2n}$[4,6]. However, by using the usual extraction method, the amount of La@$C_{74}$ is far less than that of La@$C_{82}$, which indicates that La@$C_{74}$ is more difficult to extract than La@$C_{82}$.

In view of Fig.1, we know that the intensity of La@$C_{74}$ is as 40% high as that of La@$C_{82}$, so La@$C_{74}$ is absolutely not the fragment of La@$C_{82}$. As a result, with toluene under HPHT conditions, not only La@$C_{82}$ can be extracted , but also La@$C_{74}$ can be obtained which is a new species of the soluble lanthanofullerenes.

Nevertheless, in the toluene extract, the hollow fullerenes, especially the giant fullerenes, are also increased in the same time, and the extractable species are about 0.5% of the precipitate. More efficient solvents need to be selected. Then, HPHT pyridine extraction was performed. The DEIMS of the pyridine extract is shown in Fig.2. There are peaks corresponding to La@$C_{82}$ (2n=82,80,78,76) obviously, except for La@$C_{74}$. The peak for La@$C_{82}$ is also the most intense among La@$C_{2n}$ and its intensity is almost as high as that of $C_{70.}$ Mass the extract is 14% La@$C_{2n}$ and 10% La@$C_{82}$. Furthermore, the relative intensity of the lanthanofullerenes / hollow fullerenes is higher than that of toluene. It is shown that HPHT pyridine can more efficiently dissolve lanthanofullerenes than HPHT toluene.

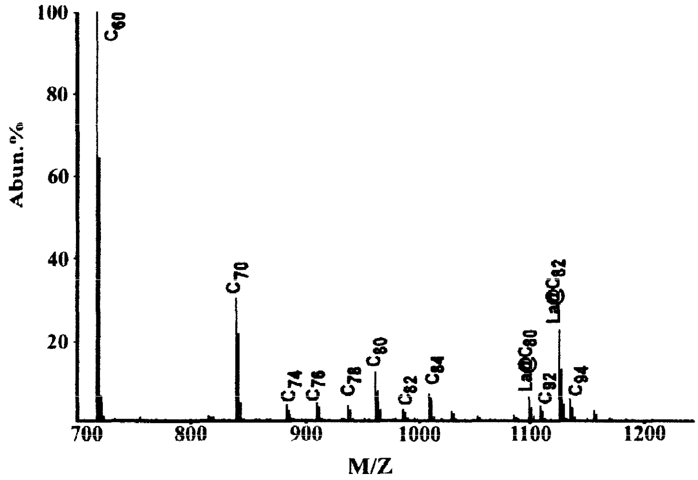

Fig.2, The DEIMS of high temperature -high pressure pyridine extract of La-containing soot produced by arc back-burning with activated anode in situ (treatment (a) ).

Besides, there is no signal of La@$C_{74}$.It is also shown that La@$C_{74}$ is less stable and more reactive that La@$C_{82}$ in pyridine. It's indicated clearly that HPHT pyridine can selectively extract metallofullerenes, especially La@$C_{82}$.

These results mentioned above were obtained from the sample produced by treatment (a). In order to get La@$C_{2n}$ as much as possible and verify the HPHT extraction method, treatment (b) was then employed. It has been reported that the carbonization of metal oxide-graphite composite rod plays an important role in the highly yield synthesis of metallofullerenes[2].

The DEIMS of pyridine extract from soot containing La@$C_{2n}$ generated by treatment (b) is shown in Fig. 3 (a). The extract are concentrated in La@$C_{82}$ and other lanthanofullerenes La@$C_{2n}$(2n=80,78,76). From the mass intensity analysis, about 80% La@$C_{2n}$ (2n=82,80,78,76) and 55% La@$C_{82}$ can be enriched which are much more than those in Fig.2. Furthermore, pyridine extractable species are weighed to be about 1% of the raw soot. It is further indicated that HPHT pyridine can be more efficiently and selectively extract lantanofullerenes, especially La@$C_{82}$.

In additional, the mass peaks near to La@$C_{82}$ are almost all corresponding to La@$C_{2n}$(2n=82,80,78,76) with only a trace of giant hollow fullerenes, such as $C_{84}$,$C_{90}$ et al., the soluble hollow species are mainly small carbon cages, such as $C_{60}$,$C_{70}$. Analysis of the mass spectral peaks intensity suggests that the average hollow fullerenes has 66 carbons. This illustrates pyridine is not fit for extraction of giant hollow fullerenes rather than lanthanofullerenes from soot. Pyridine extract facilitates to further isolate metallofullerenes in pure form, especially La@$C_{82}$, for the coming HPLC purification.

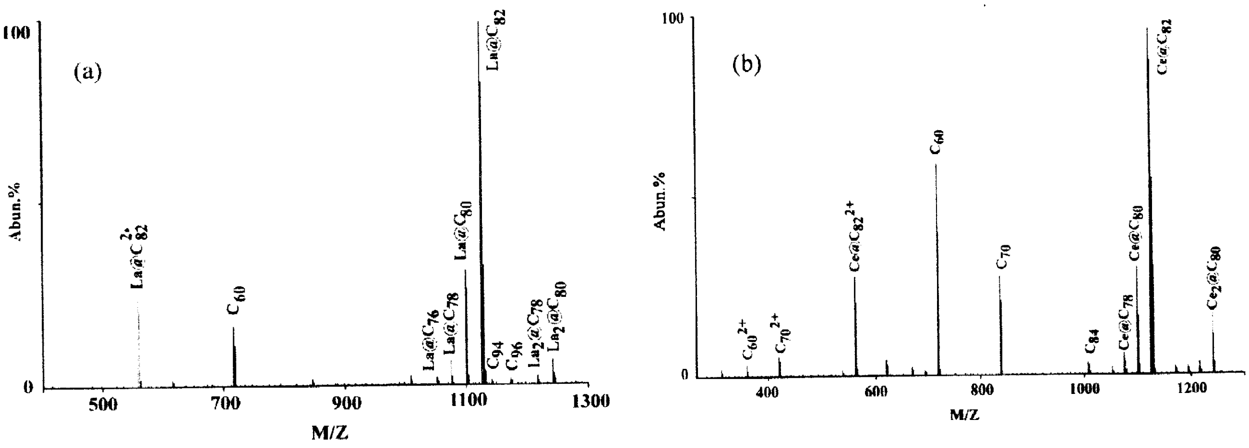

Fig.3, The DEIMS of high temperature -high pressure pyridine extract of La-containing (a) and Ce-containing (b) soot produced by arc back-burning with carbonized anode (treatment (b)).

In order to confirm the method whether fits other metallofullerenes, especially the carbon cages encapsulated with rare earth elements, soot containing Ce@$C_{2n}$ was high yield syntheized by using treatment (b) . Both toluene and pyridine extraction were performed at the same condition as that for La@$C_{2n}$ under HPHT. From the analysis of DEIMS for toluene extract , the peak for Ce@$C_{82}$ was also the most intense and that for Ce@$C_{74}$ was the second. too. Here, Ce@$C_{74}$ , is added a new soluble membership into metallofullerenes. This result is similar to toluene extract containing La@$C_{2n}$. In the DEIMS of pyridine extract (about 1% of the raw soot) shown in Fig. 3 (b), the peaks distribution is almost same as that in Fig.3(a). About 60% Ce@$C_{2n}$ and at least 35% Ce@$C_{82}$ was enriched.

It is further indicated that metallofullerenes can be efficiently and selectively extracted by different solvents under high pressure and high temperature conditions.

## Conclusion

Metallofullerenes can be efficiently extracted from the insoluble part of the soot after toluene Soxhlet extract by the high temperature-high pressure method (about 220 °C,100 atm). With pyridine as HPHT solvent, about 60-80% $M@C_{2n}$ and about 30-55% $M@C_{82}$ can be enriched, $M@C_{82}$ is selectively dissolved, the whole extractable species are about 1% of the raw soot; With toluene as HPHT solvent, $M@C_{2n}$ can also be efficiently extracted, specially $M@C_{74}$, which is added a new member of soluble species into $M@C_{2n}$.

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