Toward Efficient Synthesis of Endohedral Metallofullerenes by Arc Discharge of Carbon Rods Containing Encapsulated Rare Earth Carbides and Ultrasonic Soxhlet Extraction

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We have modified the conventional procedures for endohedral metallofullerene production by (1) arc discharge of carbon rods containing carbon-coated rare-earth carbides and (2) ultrasonic Soxhlet extraction (USE) of the raw soots. The enhanced efficiency of endohedral metallofullerene production due to the modifications above is demonstrated by high-performance liquid chromatography (HPLC) through the synthesis of the rare-earth monometallofullerenes Er@C_{82} and Pr@C_{82}.

Introduction

Endohedral metallofullerenes are normally produced by arc-burning composite rods consisting of metal oxides and graphite in a He atmosphere below 1 atm. The resulting soot is then subjected to solvent extraction, followed by HPLC isolation of the target endohedral metallofullerenes. The metallofullerene yield after the above tedious procedures is very low, e.g., far below 1% of the starting material.[1−4] It is thus extremely important to develop high-yield synthetic methods for these endohedral metallofullerenes.

To increase the metallofullerene yield, Bandow et al. used a fullerene arc generator equipped with an anaerobic sampling attachment.[5] It was found that the yield of lanthanofullerenes increased when LaC_2-enriched composite carbon rods were used for the generation of soot. Saito et al. investigated the optimum conditions for the arc synthesis of La@C_{82} by using the ESR technique.[6] The yield of La@C_{82} varied sensitively with the pressure of He buffer gas. A maximum metallofullerene yield was obtained at ∼200 Torr of He, as is the case for empty higher fullerenes. Mieno attempted to produce endohedral metallofullerenes in a gravity-free arc discharge chamber by means of a 12 m high vertical swing tower.[7] What was confirmed is the effect of gravity-free condition, which suppresses thermal convection of hot gas in the arc region and sustains long-duration reaction of the hot carbon molecules. As a result, the yield of lanthanum metallofullerene (La@C_{82}) under the gravity-free condition increased significantly compared with that under gravity of the earth.

Aside from optimization of arc-discharge conditions, improvement of solvent extraction is equally important to the metallofullerene yield given the low concentration of endohedral metallofullerenes in the raw soot. As noted by Capp et al.,[8] the question of extraction is not so much an issue of solubility alone. Metallofullerenes are actually adsorbed and trapped in the highly aggregated network of soot particles. The high-temperature, high-pressure “bomb” method was developed to coax La@C_n away from the fullerene-laden soot for n from 74 to 90. This method and its variant, although successful to some extent,[9,10] did not attract widespread use, due partially to its scale limitation, safety concerns, and unclarified mechanism. The solvent-free high-temperature sublimation method was used by Diener et al.[11] to prepare uranium endohedral metallofullerenes in an anaerobic environment. This technique exploits the differing interaction strengths of empty fullerenes and metallofullerenes with their environment in the soot. Although sublimation is inherently simple and cost-effective, a sophisticated apparatus and careful operation are needed.

In the present work, we explored the application of the soot and cathode deposit containing carbon-coated rare-earth carbide as arc-discharge starting materials to increase the metallofullerene yield. Moreover, we modified a Soxhlet extractor by incorporating ultrasonic irradiation for enhancing the metallofullerene extraction efficiency.

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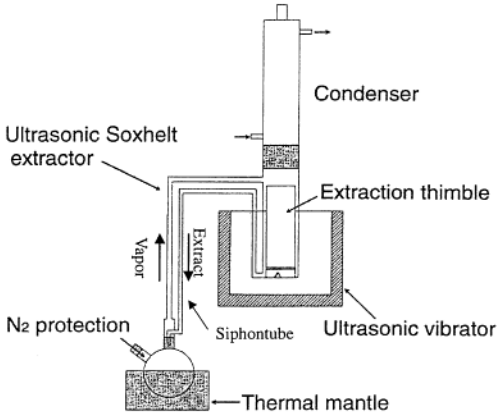

Figure 1. Schematic drawing of the ultrasonic Soxhlet extractor used for the extraction of metallofullerenes.

Experimental Section

The production of metallofullerenes containing lanthanide metal atoms was carried out in a Kratchmer−Huffman type fullerene generator.[12] Carbon rods (6 mm diameter, 10 cm long) were drilled (4.5 mm diameter) and filled with 60 wt % Er_2O_3 and 40 wt % graphite powder. To remove any adsorbed impurities and carbonize organic species, the filled carbon rods were subjected to high-temperature (1100 °C) treatment in a furnace for 3 h. The two carbon electrodes were electrically contacted with a current of 85 A under vacuum for 20 min as an in situ activation process. The preset discharge conditions were kept constant throughout, i.e., current 85 A, He pressure 125 Torr. After discharge,[5] the soot was collected for extraction or for arc redischarge, while the cathode deposit and the debris on the bottom of the chamber were well-ground and repressed quickly into the central holes of carbon rods for arc redischarge so as to minimize oxidation of the rare-earth carbide. Other procedures and arc conditions are the same as the previous runs.

A homemade ultrasound assisted Soxhlet extraction apparatus was used to extract metallofullerenes (model B1210E-MTH, 47 kHz, 143 W, Branson Ultrasonic Corp., USA) (Figure 1). The extraction solvent was DMF (*N*,*N*-dimethylformamide).[13] Slow-type filter papers (38.5 cm diameter, Whatman Paper Ltd.) were used to wrap the carbon soot for extractors in order to avoid or minimize leakage of tiny carbon soot particles. After extraction for a specified period (10, 15, or 24 h for different experiments), the extract solution was filtered before cooling down to room temperature through a slow-rate filter paper repeatedly until the solution became transparent. The resulting DMF solution was vacuum-evaporated, and the powder obtained was dissolved in toluene (∼150 mL) immediately. To facilitate the dissolution of the extract in toluene, we placed the flask containing the extract and toluene in an ultrasonic bath. After ultrasonic agitation for 10 min, the toluene solution was filtered using slow-rate filter paper, concentrated to ∼25 mL, and then passed through a 0.2 μm disk filter (Rubbermaid, Inc.) before HPLC separation.

HPLC separation was performed in Waters 600-486 system equipped with a semipreparative column (PYE Cosmosil, Nacalai Tesque, Inc., i.d. 10 × 250 mm). Toluene was used as the mobile phase. The injection volume was 5 mL, and the elution rate was 4.0 mL/min. DCI negative ion mass spectrometry (Finnigan TSQ 7000) with methane was employed for characterizing the sample compositions. High-resolution SEM for the carbon deposit and the soot was conducted in an instrument JEOL 6300F operated at 5 or 15 kV. The soot for SEM was pressed into thin pellets (1−2 mm thick) under ∼12 tons/cm^2. High-resolution TEM was carried out in a JEOL 2010 transmission electron microscope operated at 200 kV. For preparation of TEM samples, cathode deposit or soot debris on the bottom part of the arc chamber was well ground and dispersed in ethanol by sonication, followed by deposition on a holey carbon-coated copper grid. XRD experiments were conducted using a PW1830 (Phillips) X-ray diffractometer with the Cu Kα radiation source.

Results and Discussion

Arc Redischarge. Figure 2a,b displays bright-field high-resolution TEM images of the soot collected from the bottom of the chamber, showing clearly erbium carbide nanocrystals encapsulated in carbon cages. It can be seen (Figure 2a) that about half of the ployhedral carbon shells were filled or partially filled with the carbides, and the sizes of the encapsulated particles range from 20 to 50 nm, consistent with SEM observations. The encapsulated carbides are essentially single crystals as shown in an enlarged picture (Figure 2b). The observed lattice fringe spacings from several high-resolution images of the encapsulated carbide corresponds to the interplane spacings of the (101), (222), and (110) planes of tetragonal erbium dicarbide.[14] Shown in Figure 2c is a high-resolution TEM image for a sample from the cathode deposit. Besides the carbide encapsulated in polyhedral carbon cages, carbon nanotubes with or without the carbide inside were also found in the cathode deposit sample. The soot samples collected from side wall and ceiling of the arc chamber are similar to those in Figure 2a,b but with more amorphous carbon (not shown). Similar results were obtained for encapsulated α-LaC_2 inside carbon cages found by Ruoff et al.,[15] α-CeC_2 by Yosida,[16] and α-GdC_2 by Subramoney et al.[17]

Shown in Figure 3 are X-ray diffraction patterns of three materials which were used to make the composite carbon rods for arc burning: (a) a mixture of graphite powder (40 wt %) and Er_2O_3 (∼60 wt %) after heat treatment at 1100 °C in a vacuum, (b) a cathode deposit after grinding, and (c) soot and debris deposited on the bottom of the arc chamber. As shown in Figure 3a, the mixture after heat treatment at 1100 °C consists of only graphite powder and the oxide, and no carbide was observed. This is understandable because the solid-state reaction between carbon and lanthanum oxide should occur at a much higher temperature ($\geq$2000 °C).[5,18] One alternative but more effective way to convert oxide to carbide is through arc burning since the temperature of the arc region is believed to be as high as 3500 °C.[12,19] Practically, arc discharge has already been utilized to prepare lanthanum carbide.[19] As shown in Figure 3b,c, after discharge, the carbide peaks appeared while the oxide peaks decreased. Another feature in Figure 3b,c is that an extra peak on the left of the graphite (111) diffraction peak (marked with "@") appeared after

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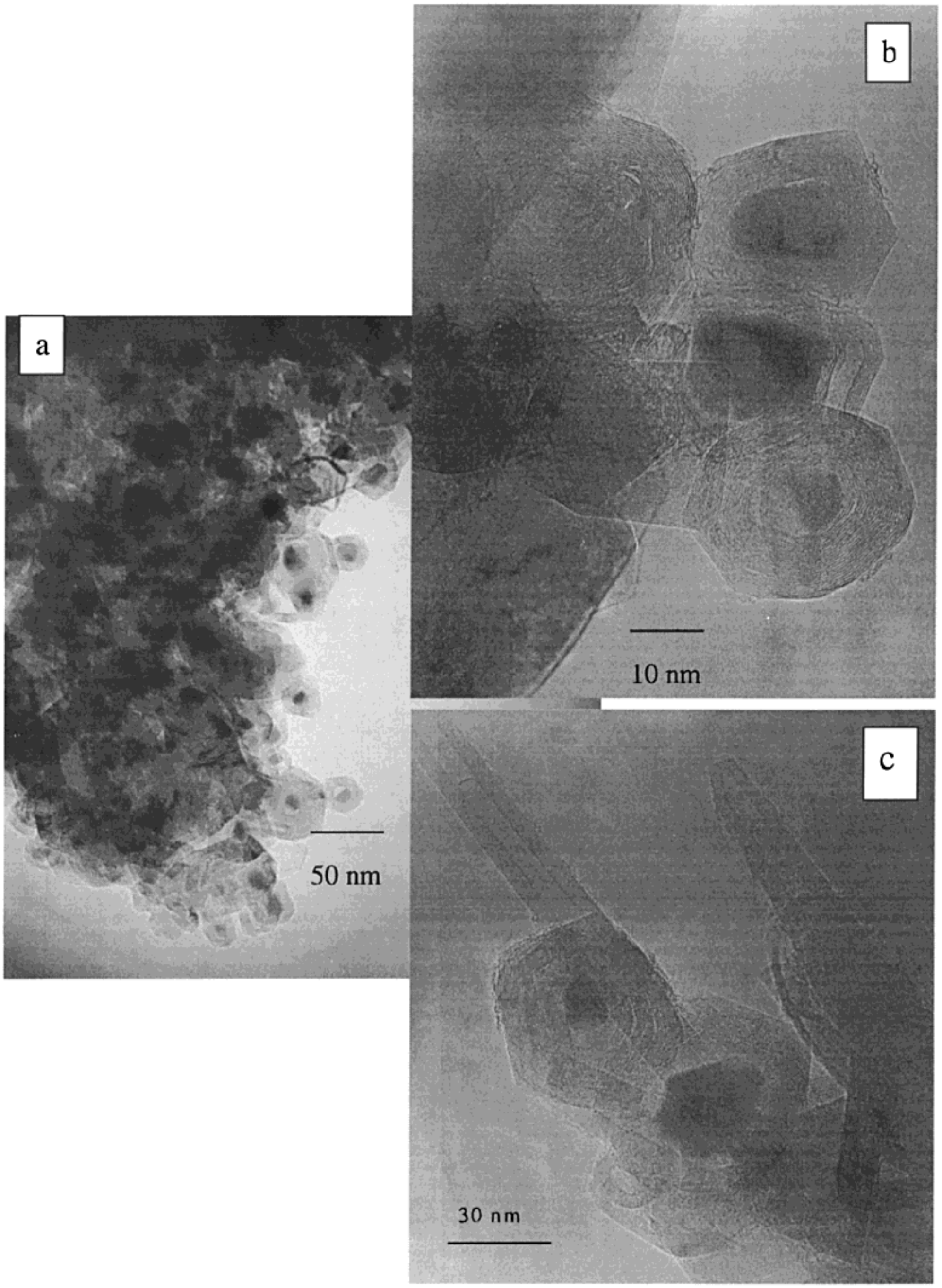

Figure 2. High-resolution TEM images of a sample collected on the bottom part of the arc chamber (a). (b) Enlargement of (a), showing the encapsulation of erbium carbide in carbon cages. (c) High-resolution TEM image for a sample from the cathode deposit containing erbium carbide. Notice the existence of carbon nanotubes and carbon-coated carbides.

discharge. This peak is attributable to the onionlike structure of graphite balls.[20] One major advantage of generating carbide through arc burning is that a large part of the carbide can be encapsulated inside the carbon onionlike cages as illustrated in the high-resolution TEM images in Figure 2, which prevent the carbide from being reoxidized.

However, because the percentage of the oxide is pretty high (60 wt %) in the starting materials, some carbides may have not been encapsulated into the carbon cages and therefore easily reoxidized. The oxides observed in the XRD profiles of the cathode deposit and the soot in the bottom of the chamber are from reoxidation of the nonencapsulated carbides for two reasons. First, the temperature in the arc region is not sufficiently high to convert the all the oxide to carbide. Second, because the nonencapsulated carbide is very unstable in air, its reoxidation was not completely avoided due to the fact that we did not do any special protection for the samples when we ground the samples and performed X-ray diffraction measurements on these samples.

The cathode deposit and soot in different parts of the arc chamber account for ~60% in weight of the total discharged materials, and we explored the potential of

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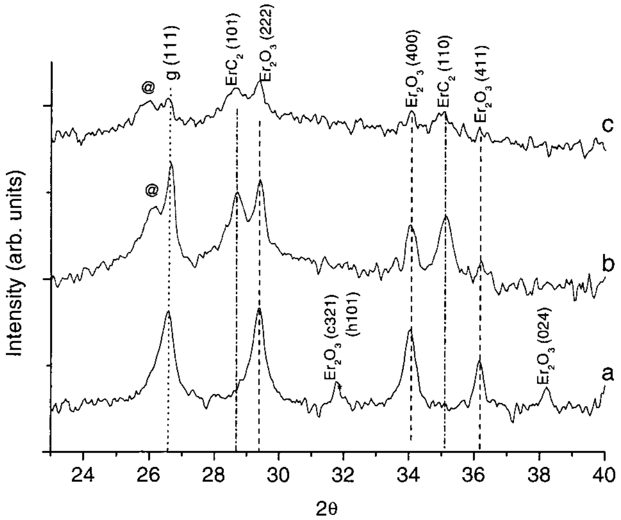

Figure 3. X-ray diffraction patterns for (a) mixture of graphite power (40 wt %) and Er_2O_3 (60 wt %) after heat treatment at 1100 °C, (b) well-ground cathode deposit, and (c) soot deposited on the bottom of the arc chamber. "@" indicates the diffraction peak corresponding to the onion structure of graphite, and "g" marks the graphite diffraction peaks.

these materials for arc redischarge for enhancing metallofullerene yield. In this work, HPLC was used not only to isolate but also to estimate the amount of the metallufullerenes. To make meaningful comparisons, identical conditions were adopted in different extraction runs: the same amount of soot for extraction, the same extraction procedures and time, the same final volume for HPLC isolation, and so on. A typical HPLC trace for the soot extract from the heat-treated carbon rods filled with erbium oxide and graphite powder is shown in Figure 4a. The peak of Er@C_{82} appears at ~24.5 min. We use the peak height to roughly represent the relative amount of the metallofullerene.

By arc redischarge of the composite rods containing the cathode deposit and the debris on the bottom of the arc chamber, the yields of metallofullerenes as well as empty fullerenes are significantly enhanced under the same discharge and posttreatment conditions. As shown in Figure 4b (from discharge of the cathode deposit) and Figure 4c (from discharge of the debris on the bottom of the arc chamber), the HPLC peaks of Er@C_{82} are surprisingly strong and are in fact oversaturated. The solutions, after dilution, were reinjected into HPLC. In this way, we estimated the "peak height" of the oversaturated peaks of Er@C_{82} in Figure 4b,c to be approximately 1 order of magnitude higher than that from the soot without arc redischarge (Figure 4a). By arc redischarge, we can obtain 3−8 mg of metallofullerenes with purity higher than 95% (judged from DCI mass spectra) for each run of 10 filled carbon rods. We also tried the residual soot after extraction as arc-discharge material and obtained similar results. Suffice it to say, we have found not only a route to produce metallofullerenes more efficiently but also a route to convert the expensive "wastes" to recyclable materials.

The formation of metallofullerene in the arc plasma region is believed to involve metal carbide precursors. The presence of oxygen atoms probably impedes the formation of the metal carbide precursors. In addition, the high bond strength of C−O (1076.5 kJ/mol[21]) will also hinder the closing of carbon cages (C−C 607 kJ/mol). Therefore, fullerenes and metallofullerenes are formed in low yield. Finally, even if metallofullerenes were formed occasionally in the presence of oxygen, these cages might be damaged by oxygen due to oxygen sensitivity of metallofullerenes as a narrow band gap molecule. The absence or dilution of oxygen in the cathode deposit and the soot due to the conversion of oxide to carbide and the use of encapsulated carbide as a precursor therefore results in a high yield of endohedral metallofullerenes through arc redischarge.

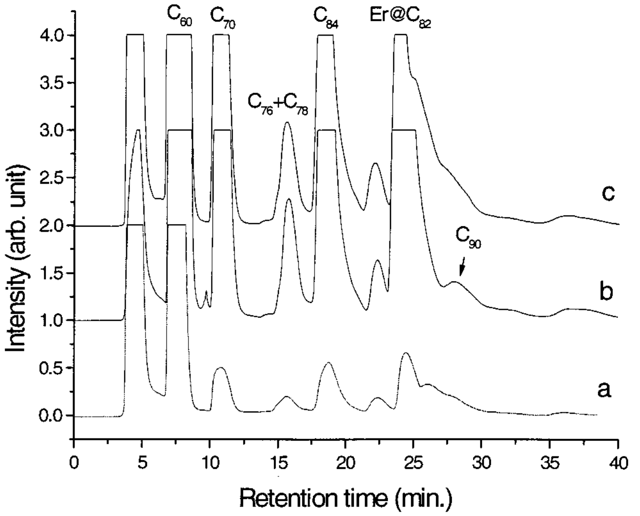

Figure 4. Typical HPLC traces for soot extracts generated from different precursors: (a) carbon and Er oxide, (b) cathode deposit, and (c) soot and debris deposited on the bottom of the chamber. The injection volume is 5 mL. Traces b and c are displaced vertically for clarity from trace a.

Ultrasonic Soxhlet Extraction. In our home-built ultrasonic Soxhlet extraction system (Figure 1), similar to traditional Soxhlet extraction, the DMF vapor goes up with the assistance of nitrogen gas and condenses in the condenser. The solution containing metallofullerenes returns to the flask through a siphon tube in a time interval of ~25 min. As observed through the siphon, the solution color from extraction with ultrasonic agitation is much deeper than that without ultrasonic agitation, indicating the higher efficiency of the ultrasonic Soxhlet extractor. After 3−4 h of extraction, termination of the ultrasonic irradiation resulted immediately in the faded color of the extracted solution as observed from the siphon tube. In this case, the extraction essentially becomes traditional Soxhlet extraction. In the traditional Soxhlet extraction, one may take the faded color as an indication that the metallofullerenes had been fully extracted. The solution in the siphon tube, however, was deep-colored again once the ultrasonic irradiation was resumed.

In the traditional Soxhlet extraction of fullerenes and metallofullerenes, it is generally believed that the extent of extraction can be over 90% after 10 h of recycling,[13,22,23] and therefore the carbon dregs were dis-

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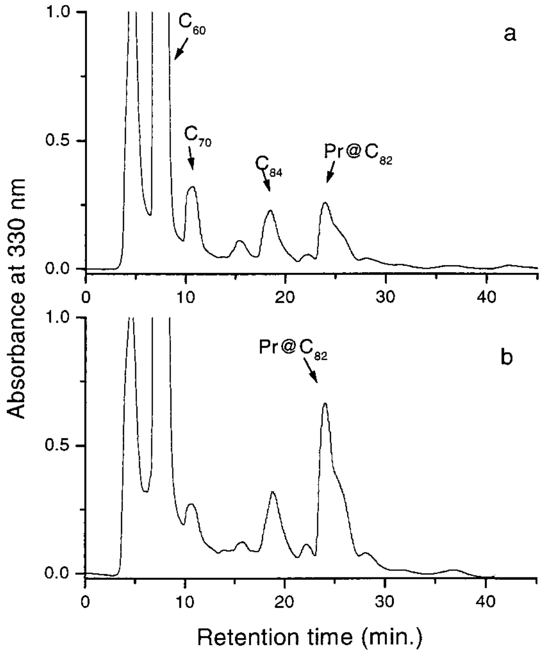

Figure 5. (a) HPLC chromatogram of the Pr extract (dissolved in 20 mL of toluene) from TSE of raw soot (DMF was the extraction solvent) for 15 h. (b) HPLC chromatogram of the Pr extract (dissolved in 20 mL of toluene) from USE of the sample in (a) for another 15 h. Note that more $Pr@C_{82}$ was extracted even though the soot had been extracted by TSE for 15 h.

carded. However, due to strong adsorption,[24] ready aggregation,[25] and shielding effect of carbon soot, the metallofullerenes are actually far from fully extracted after extraction for only 10 h. Figure 5 demonstrates the effect of ultrasonic irradiation on the metallofullerene extraction using HPLC. For comparison of the samples obtained without USE and with USE, the volumes of the extraction solvent (180 mL) and the toluene solution (20 mL) before HPLC separation were kept the same. The injection volume was also fixed to 5 mL for both analyses. Remarkably, the quantity of $Pr@C_{82}$ from USE (Figure 5b) is about 2 times that from TSE (Figure 5a). It is estimated that the traditional Soxhlet extractor extracted less than 35% metallofullerene in 15 h. Evidently, the ultrasound assisted Soxhlet extraction increases the extraction extent significantly.

For the sake of a more meaningful comparison on the performance of the two extractors, we monitored the extraction processes by HPLC in 10 h intervals under the same extraction conditions except that one was with USE and the other was with TSE. In this case, Er-containing carbon soot (~10 g for each run) was used. The results are shown in Figure 6. The amount of $Er@C_{82}$ extracted during the first 10 h by USE is much larger than that by TSE. The extractable $Er@C_{82}$ decreases gradually for TSE but decreases sharply for USE. After 30 h extraction, over 90% of the metallofullerene was extracted by USE, whereas only ~50% was extracted by TSE.

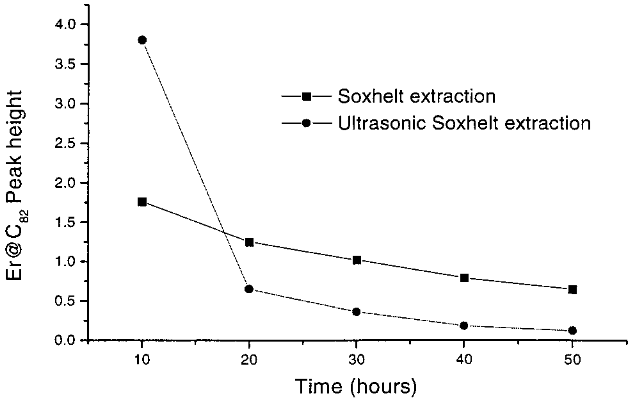

Figure 6. HPLC peak height of $Er@C_{82}$ vs extraction time for both the ultrasonic Soxhlet extractor and the traditional Soxhlet extractor.

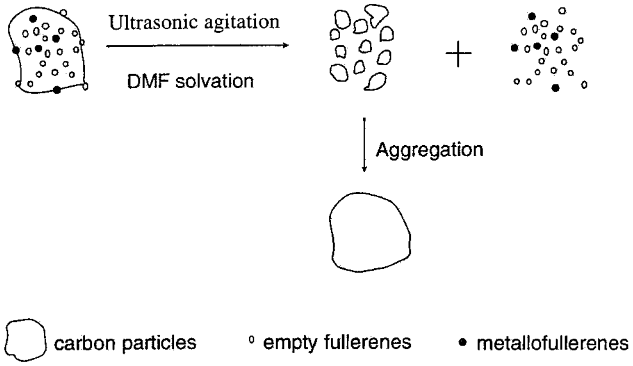

Figure 7. Proposed model for the process of extraction and separation of metallofullerenes under ultrasonic irradiation.

The improved extraction efficiency using USE suggests that the extraction of metallofullerenes from carbon soot is not only a question of solubility but also very much related to the adsorption and trapping of the metallofullerene cages on the nanoscale carbon matrix. The ultrasonic agitation has the effect of desorbing and detrapping the metallofullerenes from the carbon nanoparticle matrix. In fact, the USE method was shown to be efficient for the extraction of polychlorinated aromatic compounds.[26] Figure 7 gives a model for the process of extraction and separation of metallofullerenes under ultrasonic irradiation. The key point of this model is that carbon particle aggregates (most likely sintered together) containing metallofullerenes are broken down into smaller pieces by ultrasonic irradiation. One consequence is that the metallofullerenes on the nanocarbon surfaces become more exposed to the extraction solvent. Second, the dissolved metallofullerenes will not be easily readsorbed by the dispersed carbon particles under ultrasonic irradiation. In addition, local heating by the ultrasound may also have the effect of enhancing the dissolution of metallofullerenes. However, in the traditional Soxhlet extractor, the carbon nanoparticles remain in an aggregated form, and the metallofullerenes dissolve in the solvent primarily through a diffusion process. Given the strong aggregation tendency of the nanoscale carbon particles in arc discharge, most metallofullenes are believed to be trapped inside the aggregates and therefore difficult to extract just by diffusion. Ultrasonic irradiation mobilizes the metallofullerenes away from the surface of tiny carbon particles

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so that the extraction extent and efficiency are both improved.

Concluding Remarks

We have demonstrated with HPLC analysis that the yields of metallofullerene are about 1 order of magnitude higher for samples produced from carbon-coated rare-earth carbide-enriched materials than from the pristine rare-earth oxides. The arc-treated materials (cathode deposit, debris on the bottom of the chamber, soot before extraction and after extraction) containing abundant carbon-coated carbide are found to be much better than the mixture of oxide and carbon powder as arc-discharge starting materials for macroscopic synthesis of endohedral metallofullerenes. The absence of oxygen atoms, which impede the formation processes of metallofullerenes, is believed to account for the higher yield synthesis.

The ultrasonic Soxhlet extraction technique was successfully applied for the first time to extract endohedral metallofullerenes in an efficient way. Through the comparative studies of the new extractor and traditional extractor, we found that more metallofullerenes still remain in carbon soot after 15 h extraction using a traditional one, whereas ultrasound-assisted Soxhlet extraction is superior in metallofullerene extraction efficiency.

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