High-Yield Extraction of Endohedral Rare-Earth Fullerenes

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The technique of high-temperature high-pressure extraction with pyridine has been successfully utilized to extract a wide variety of endohedral rare-earth fullerenes of the type $Ln@C_{2n}$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb). $Ln@C_{80}$, $Ln@C_{82}$, and $Ln_2@C_{80}$ for most of the rare-earth metals can be produced with high-yield and selectively extracted from the carbon-arc evaporation soot. Metallofullerenes containing Sm, Eu, and Yb (which could have +2 oxidation states) are especially difficult to extract. Some possible reasons for the high-yield extraction are discussed. The laser desorption mass spectrometric characterization results indicate a relationship between the extraction yields of metallofullerenes and the oxidation states and ionic radii of the rare-earths.

Introduction

The synthesis and extraction of endohedral metallofullerenes have attracted considerable research interest because they are very important for the further investigation of the physical and chemical properties, molecular structures, and some interesting applications of metallofullerenes as a new type of superconductors, organic ferromagnets, magnetic resonance imaging agents, and so on.[1] Since the first examination of $La@C_{2n}$ using a laser vaporization technique,[2] a great deal of work has been done to produce endohedral metallofullernes.[3−10] Chai *et al.* reported the first macroscopic amount of metallofullerenes by laser vaporization of a graphite−metal composite in a helium-filled tube-oven at a high temperature.[3] Subsequently $Y@C_{2n}$,[4] $U@C_{2n}$,[5] and $Ca@C_{60}$[6] were successfully produced by this technique. An increasing variety of metallofullerenes with Sc, Y, and most of the lanthanid elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er) encapsulated into the empty all-carbon frameworks have been successfully synthesized in bulk by arc evaporization and resistive heating methods.[7−10]

Nevertheless, the production yield is limited by the scant solubility of metallofullerenes, which is similar to that of giant fullerenes. These species dissolve better in pyridine than in CS_2 or toluene.[11,12] The usually used toluene Soxhlet extraction gives relatively low yields for metallofullerenes.

High-temperature, high-pressure extraction with toluene has proved to be effective for the extraction of $La@C_{2n}$ and some giant empty fullerenes.[13−15] Considering the better solubility of metallofullerenes in pyridine, pyridine high-temperature, high-pressure extraction of metallofullerenes was used in this experiment. A wide variety of endohedral rare-earth metallofullerenes can be selectively extracted using this method, as we report in this paper.

Experimental Method

A standard fullerene generator was used for the preparation of metallofullerene soot. In each case, graphite rods ($\phi = 6 \times 100$ mm) were drilled out ($\phi = 4 \times 70$ mm) and filled with a mixture of metal oxides and carbon powder. The metal oxides used in this experiment were as follows: La_2O_3 (99.99%), CeO_2 (99.99%), Pr_6O_{11} (99.99%), Nd_2O_3 (99.99%), Sm_2O_3 (99.99%), Eu_2O_3 (99.99%), Gd_2O_3 (99.99%), Tb_4O_7 (99.99%), Dy_2O_3 (99.99%), Ho_2O_3 (99.99%), Er_2O_3 (99.99%), Tm_2O_3 (99.99%),

and Yb_2O_3 (99.99%). The metal oxides were dried under vacuum at 300 °C for 5 h before being used. The atomic ratio of C/Ln was 100:1 for all metals in order to compare the results. The graphite rods with the mixture filled inside were baked under vacuum at 1800 °C for 3 h.

Prior to arc burning, the synthesis chamber was pumped to 2.5 Pa and the graphite anode was electrically contacted with the graphite cathode and a current of 200 A was passed through for 20 min as an *in situ* activating process. This has proved to be helpful for the high-yield synthesis of $La@C_{2n}$.[16] During the arc burning, the graphite anode was consumed within 40 min, then the arc polarity was reversed for "back-burning" to increase the yield of metallofullerene species.[17] The resultant soot was collected and Soxhlet extracted for 5 h with toluene. The toluene extracts were dark purplish red. The residual soot was then dried prior to high-temperature, high-pressure extraction.

A 50 mL stainless steel tube was carefully chosen such that if every carbon atom in the soot were changed into CO_2 and if the solvent changed into gas phase, the pressure would not be enough to break the stainless steel tube. About 40 mL of pyridine was added to 10 mg of soot, resulting in a sludge. The mixture was stuffed into the stainless steel tube. Nitrogen was flowed into the mixture for about 1 h to get rid of any dissolved oxygen. The tube was then sealed under N_2 and baked at 200 °C for 5 h. It was then taken out and opened after cooling. The resultant dark-black sludge was filtered and washed to remove any insoluble carbon soot. The resultant pyridine high-temperature, high-pressure extracts were dark brown.

The extracts were analyzed by laser desorption−ionization time-of-flight mass-spectrometry (LDI/TOF/MS, MALDI-1700, Biochemistry Instrument Co., Ltd.). A nitrogen laser (wavelength 337 nm) was used to desorb and ionize the species. The laser beam was attenuated to very low energy (about 3−5 μJ) to avoid unnecessary fragmentation. More than 30 laser shots were used for each sample.

Results and Analysis

The laser desorption (LD) mass spectra of the toluene Soxhlet extracts show weak peaks corresponding to a wide variety of rare-earth metallofullerenes together with dominant empty fullerene species containing an even number of carbon atoms. The spectra of La, Ce, Sm, Eu, Gd, Tb, and Ho toluene extracts are similar to some previous reports.[9,10]
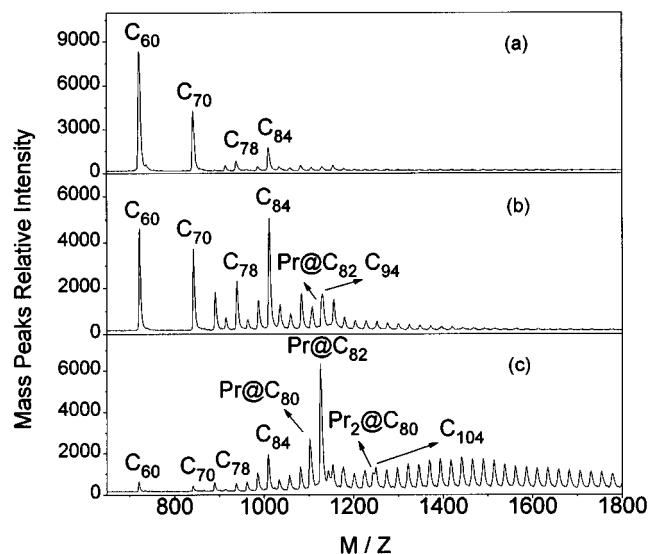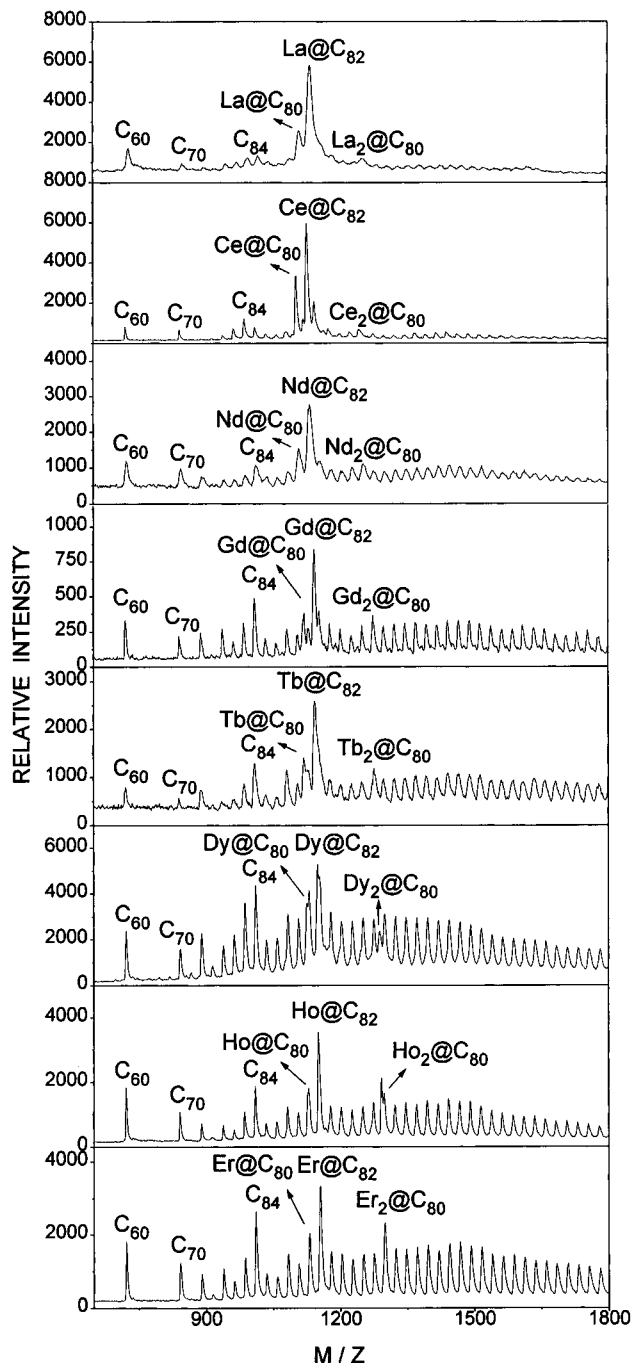
Figure 1. LD mass spectra of extracts obtained from soot produced by the arc-burning of carbon rods containing the rare-earth oxide Pr_6O_{11}: (a) toluene Soxhlet extract at its boiling point, (b) toluene extract at high temperature, high pressure, (c) pyridine extract at high temperature, high pressure.

The LD mass spectra of the toluene Soxhlet extracts containing Pr^-, Tm^-, and Yb^- metallofullerenes have not been reported before. The spectra of Pr^- metallofullerenes, for example, are shown in Figure 1 for (a) the toluene Soxhlet extract at its boiling point, (b) the toluene high-temperature, high-pressure extract at 200 °C, and (c) the pyridine high-temperature, high-pressure extract at 200 °C. As seen in Figure 1, the intensity of the peak corresponding to $Pr@C_{82}$ is very small in the LD spectra of the toluene extracts, which indicates that it is difficult to extract using toluene, even under high-temperature, high-pressure conditions. However, it can be selectively extracted with high-yield from empty fullerenes and other size metallofullerenes by pyridine.

The LD mass spectra of pyridine extracts of other metals are divided into two categories according to their different intensities of $Ln@C_{82}$ and $Ln_2@C_{80}$. The LD spetra for the case of La, Ce, Nd, Gd, Tb, Dy, Ho, and Er are shown in Figure 2 and those of Sm, Eu, Tm, and Yb are shown in Figure 3. In Figures 2 and 3, the drop of the relative intensities of empty fullerenes C_{60} and C_{70} is largely due to the dissolving of fullerenes into toluene. A series of giant empty fullerenes C_{2n} for $2n$ from 74 to 200 can be detected. As seen in Figure 2, the metallofullerenes series, *i.e.* $Ln@C_{80}$, $Ln@C_{82}$, and $Ln_2@C_{80}$, of each element can be observed with high intensity, indicating that they have been extracted with high yield from the soot. The approximate yields of metallofullerenes in pyridine extracts can be estimated by weighing the soot loss after extraction and calculating $Ln@C_{2n}/C_{2n}$ ratios presented in the mass spectra. For $Ce@C_{2n}$ as an example, after pyridine high-temperature, high-pressure extraction, the carbon soot lost about 0.6% of the primary soot weight (most of the empty fullerenes were extracted by toluene), since $Ce@C_{2n}$ is more than 75% in the mass spectra, their yields should be approximate 0.45% of the primary soot. In contrast, Figure 3 shows only weak peaks corresponding to Sm-, Eu-, Yb-, and $Tm@C_{82}$. No peaks corresponding to Sm-, Eu-, or $Yb_2@C_{80}$ are observed. The relative intensity ratios of $M@C_{82}$ to C_{60} and some physical properties of rare-earth metals are listed in Table 1.[18]

Discussion and Conclusions

Why is the high-temperature, high-pressure extraction of pyridine so effective for the extraction of metallofullerenes? First

Figure 2. LD mass spectra of pyridine high-temperature, high-pressure extracts obtained from soot produced by the arc-burning of carbon rods containing the rare-earth oxides La_2O_3, CeO_2, Nd_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, and Er_2O_3.

of all, it is reasonable to believe that the solvation of metallofullerenes is a thermally activated process, as it is for some giant empty fullerene species.[19] High-temperature would then be helpful for the further solvation of metallofullerenes. Secondly, the polarity of the solvent is another important factor governing extraction efficiency. The encapsulating of the metal ions enhances the molecular polarity of $M@C_{2n}$ compared to the empty fullerenes, thus making $M@C_{2n}$ more soluble in the polar solvent pyridine than in toluene. The relative solubility of metallofullerenes in different solvents is pyridine $> CS_2 >$ toluene, while the solubility of C_{60} in different solvents is CS_2 $>$ toluene $>$ pyridine. The differences between the solubilities maybe one reason why some stable metallofullerenes species such as $M@C_{82}$ and $M_2@C_{80}$ could be selectively extracted with high yield.

Endohedral Rare-Earth Fullerenes

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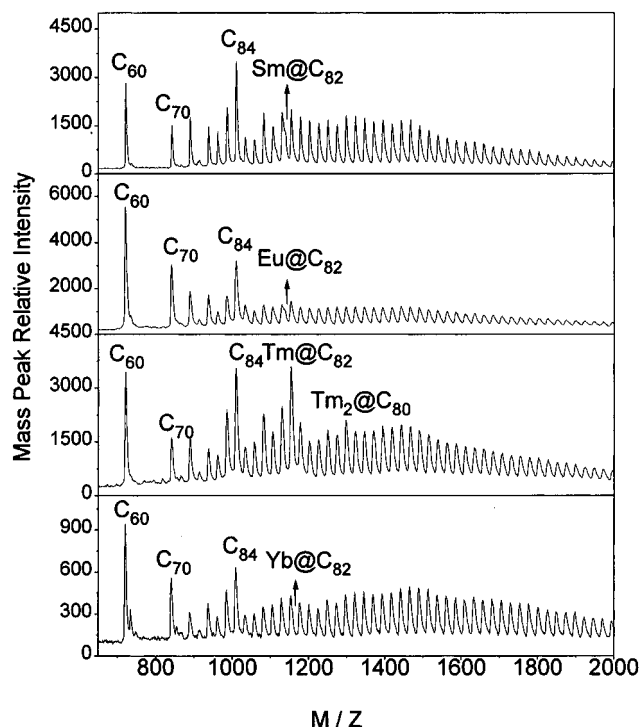
Figure 3. LD mass spectra of pyridine high-temperature, high-pressure extracts obtained from soot produced by the arc-burning of carbon rods containing the rare-earth oxides Sm_2O_3, Eu_2O_3, Tm_2O_3, and Yb_2O_3.

TABLE 1: Physical Properties of Rare-Earth Metals and Relative Ratio of $M@C_{82}:C_{60}$[a]

element	electronic config	oxide	oxid states	ionic radii (pm)	MW of $M@C_{82}$	$M@C_{82}:C_{60}$
La	$[Xe]5d6s^2$	La_2O_3	+3	106.1	1123	4.54
Ce	$[Xe]4f5d6s^2$	CeO_2	+3 +4	103.4, 92	1124	9.21
Pr	$[Xe]4f^36s^2$	Pr_6O_{11}	+3 +4	101.3, 90	1125	11.33
Nd	$[Xe]4f^46s^2$	Nd_2O_3	+3	99.5	1128	3.26
Sm	$[Xe]4f^66s^2$	Sm_2O_3	+2 +3	111, 96.4	1134	0.33
Eu	$[Xe]4f^76s^2$	Eu_2O_3	+2 +3	109, 95	1136	0.12
Gd	$[Xe]4f^75d6s^2$	Gd_2O_3	+3	93.8	1141	2.75
Tb	$[Xe]4f^96s^2$	Tb_4O_7	+3 +4	92.3, 84	1143	9.31
Dy	$[Xe]4f^{10}6s^2$	Dy_2O_3	+3	90.8	1146	2.29
Ho	$[Xe]4f^{11}6s^2$	Ho_2O_3	+3	89.4	1149	2.02
Er	$[Xe]4f^{12}6s^2$	Er_2O_3	+3	88.1	1151	1.83
Tm	$[Xe]4f^{13}6s^2$	Tm_2O_3	+2 +3	94, 86.9	1153	0.96
Yb	$[Xe]4f^{14}6s^2$	Yb_2O_3	+2 +3	93, 85.8	1157	0.24

[a] For the case of Nd, Er, and Tm, the relative intensity ratio of $M@C_{82}$ to C_{60} shown in Table 1 should be a little higher than the true value because the metal atomic weights are nearly identical to an even number of carbons: $AW_{Nd} = 144.2$ g/mol $\approx 12C$; $AW_{Er} = 167.3$ g/mol $\approx 14C$; $AW_{Tm} = 169.2$ g/mol $\approx 14C$, so the peaks corresponding to $M@C_{82}$ should be a combination of C_{2n} and $M@C_{82}$ for $Nd@C_{82}$ (1128 amu) with C_{94} (1128 amu), and $Er@C_{82}$ (1151 amu) and $Tm@C_{82}$ (1153 amu) with C_{96} (1152 amu).

The differences in relative intensities presented in the LD mass spectra suggest that the oxidation states of rare-earth elements could be important for the stability and solubility of metallofullerenes. Moro *et al.* have divided the rare-earth elements into two groups, La, Ce, Pr, Nd, Gd, Tb, Ho, Er, and Lu (group A) and Sm, Eu, and Yb (group B), according to a LD mass spectrometry study of primary soots. They proposed the oxidation state +2 for Sm, Eu, and Yb.[20] In our study, the yields of Sm-, Eu-, Yb-, and $Tm@C_{82}$ are much lower than those of other rare-earths with +3 and +4 oxidation states. It is found that the relative intensity ratios for Sm-, Eu-, Yb-, and $Tm@C_{82}$ to C_{60} are identical with the redox potentials Ln^{2+}/Ln^{3+},[18] which are shown in Table 2. The results suggest that the more stable the M^{2+} ion is, the more difficult it is for $M@C_{82}$

TABLE 2: Redox Potentials and Ratio of $M@C_{82}:C_{60}$ for Sm, Eu, Yb, and Tm

Ln	$E°_{Ln}(M^{2+}/M^{3+})$ (eV)	$M@C_{82}:C_{60}$
Eu	−0.35	0.12
Yb	−1.15	0.24
Sm	−1.55	0.33
Tm	−2.3 ± 0.2	0.96

to be synthesized and extracted. In the case of rare-earths with +3 or +4 oxidation states, the +4 metal species Ce-, Pr-, and $Tb@C_{82}$ are much more abundant than the corresponding species for metals with +3 oxidation states. More electron transfer has likely occurred between the encapsulated Ce, Pr, and Tb ions and fullerenes cages, making Ce-, Pr-, and $Tb@C_{82}$ molecules have stronger polarity and better solubility in the polar solvent.

Lanthanide contraction of the ionic radii of the metals which have stable +3 oxidation states (*i.e.* La, Nd, Gd, Dy, Ho, and Er) is thought to be related to the extraction yields of metallofullerenes. From La to Er, the yields gradually decrease with the increase of atomic numbers and decrease of Ln^{3+} ionic radii. The yields of metallofullerenes for some light rare-earth metals (La, Nd, and Gd) are found to be higher than those of heavy rare-earth metals (Dy, Ho, and Er).

The LD mass spectrometric characterization itself is affected by many uncontrolled factors. The results required more direct measures for confirmation. The study of the states of the encapsulated rare-earth ions can also be probed by NMR, ESR, XPS, and fluorescence spectroscopy techniques.

In conclusion, a new extraction technique using pyridine at high temperature and high pressure has been proved effective for the high-yield extraction of most endohedral rare-earth fullerenes. According to the relative ratios of $M@C_{82}$ to C_{60} in LD mass spectra, metallofullerenes of Ce, Pr, and Tb, which could have +4 oxidation states, are most readily extracted and those of Sm, Eu, Tm, and Yb, which could have +2 oxidation states, are more difficult to extract. The high temperature and the polarity of the solvent are believed to be important for the high-yield extraction. The oxidation state, ionic radii, redox potentials, and the lanthanide contraction are also found to correlate with the extraction yield.

Note Added in Proof. Kubozono and co-workers have reported an effective extraction of metallofullerenes $M@C_{60}$ with aniline recently.[21] Aniline was found to be very useful for the extraction of $M@C_{60}$. Because *J. Am. Chem. Soc.* usually does not arrive in China promptly, I did not know of that communication earlier. It seems reasonable to believe that aniline would also have excellent extraction effects on metallofullerenes $M@C_{82}$ and $M_2@C_{80}$, even though it was not mentioned. The aniline extraction yields of $Ce@C_{60}$ and $Pr@C_{60}$ are higher than those of other metallofullerenes, which is similar to our results.

References and Notes

(1) for recent review, Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993,** *366,* 123.

(2) Hearth, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Am. Chem. Soc.* **1985,** *107,* 7779.

(3) Chai, Y.; Guo, T.; Jin, C.; Hanfler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991,** *95,* 7564.

(4) Weaver, J. H.; Chai, Y.; Kroll, G. H.; Jin, C.; Ohno, T. R.; Hanfler, R. E.; Guo, T.; Alford, J. M.; Conceicao, J.; Chibante, L. P. F.; Jain, A.; Palmer, G.; Smalley, R. E. *Chem. Phys. Lett.* **1992,** *190,* 460.

(5) Guo, T.; Diener, M. D.; Chai, Y.; Alford, M. J.; Hanfler, R. E.; McClure, S. M.; Ohno, T. R.; Weaver, J. H.; Scuseria, G. E.; Smalley, R. E. *Science* **1992,** *257,* 1661.

(6) Wang, L. S.; Alford, J. M.; Chai, Y.; Diener, M. D.; Zhang, J.; McClure, S. M.; Guo, T.; Scuseria, G. E.; Smalley, R. E. *Chem. Phys. Lett.* **1993,** *96,* 7153.

(7) Shinohara, H.; Sato, H.; Ohkohchi, M.; Ando, Y.; Kodama, T.; Shida, T.; Kato, T.; Saito, Y. *Nature* **1992,** *357,* 52.

(8) (8) Soderholm, L.; Wurz, P.; Lykke, K. R.; Parker, P. H.; Lytle, F. W. *J. Phys. Chem.* **1992,** *96,* 7153.

(9) Johnson, R. D.; de Vries, M. S.; Salem, J.; Bethune, D. S.; Yannoni, C. S. *Nature* **1992,** *355,* 239.

(10) Gillan, E. G.; Yeretzian, C.; Min, K. S.; Alvarez, M. M.; Whetten, R. L.; Kaner, R. B. *J. Phys. Chem.* **1992,** *96,* 6869.

(11) Ross, M. M.; Nelson. H. J.; Callahan, J. H.; McElvany, S. W.; *J. Phys. Chem.* **1992,** *96,* 5231.

(12) Shinohara, H.; Sato, Y.; Ohkohchi, M.; Ando, Y. *J. Phys. Chem.* **1992,** *96,* 3571.

(13) Capp, C.; Wood, T. D.; Marshall, A. G.; Coe, J. V. *J. Am. Chem. Soc.* **1994,** *116,* 1987.

(14) Creasy, W. R.; Zimmerman, J. A.; Ruoff, R. S.; *J. Phys. Chem.* **1993,** *97,* 973.

(15) Lamb, L. D.; Huffman, D. R.; Workman, R. K.; Howells, S.; Chen, T.; Sarid, D.; Ziolo, R. *Science* **1992,** *255,* 1413.

(16) Liu, B. B.; Xu, W. G.; Liu, Z. Y.; Yang, H. B.; Li, M. H.; Liu, S. Y.; Zou, G. T. *Solid State Commun.* **1996**, *97,* 407.

(17) Bandow, S.; Shinohara, H.; Saito, Y. *J. Phys. Chem.* **1993,** *97,* 6101.

(18) Qiang, S. *The Chemistry of Rare-Earths,* 1st ed.; Zhengzhou: Henan, 1993; Chapter 1.

(19) Smart, C.; Eldridge, B.; Reuter, W.; Zimmerman, J. A.; Creasy, W. R.; Rivera, N. Ruoff, R. S. *Chem. Phys. Lett.* **1992,** *188,* 171.

(20) Moro, L.; Ruoff, R. S.; Becker, C. H.; Lorents, D. C.; Malhotra, R. *J. Phys. Chem.* **1993,** *97,* 6801.

(21) Kubozono, Y.; Maeda, H.; Takabayashi, Y.; Hiraoka, K.; Nakai, T.; Kashino, S.; Emura, S.; Ukita, S.; Sogabe, T. *J. Am. Chem. Soc.* **1996,** 118, 6998.