# In Situ Laser-Furnace TOF Mass Spectrometry of C<sub>36</sub> and the Large-Scale Production by Arc-Discharge

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A greatly improved synthesis of  $C_{36}$ , obtained as its hydrides  $C_{36}H_4$  and  $C_{36}H_6$  and oxyhydrides  $C_{36}H_4O$  and  $C_{36}H_6O$ , via a high- temperature laser vaporization (laser-furnace) method and the conventional DC arcdischarge method is reported. We have found that doping metal catalysts such as Ni/Co or Ni/Y into the laser target graphite rod or the DC arc-discharge electrode, respectively, significantly enhanced the production of  $C_{36}$  species; the methods have been known for efficient production methods of single-wall carbon nanotubes (SWNTs). The results suggest that the catalytic formation of  $C_{36}$  species and SWNTs is closely related with each other in their early stage of formation. Furthermore, a molecular  $C_{36}H_6$  gives  $C_{18}H_3$  (m/z = 219) as a magic fragment upon desorption/ionization. By using a high-performance liquid chromatography (HPLC),  $C_{36}H_6$  was purified (99%) in milligram quantity for the first time. The purified  $C_{36}H_6$  exists as a clusterassembled material such as oligomers or clusters in the solid state, not as a molecular crystal such as  $C_{60}$ .

#### Introduction

 $C_{60}$  has been considered as the smallest fullerene having the cage-structure that can be produced, separated, and isolated in a macroscopic quantity ever since Krätschmer and Huffman's first macroscopic production of fullerenes.<sup>1</sup> This is largely because of the fact that  $C_{60}$  is the smallest fullerene which satisfies the so-called isolated pentagon rule (IPR).<sup>2</sup> Some fullerenes and metallofullerenes smaller than  $C_{60}$ , such as  $C_{20}$ ,  $C_{28}$ , and  $M@C_{28}(M = U, Ti, etc.)$ , were found to be stable in gas-phase cluster-beam experiments<sup>3</sup>, and their structures have been predicted by theoretical calculations.<sup>4–6</sup> However, the bulk production and the isolation of these materials have not been successful, and thus the extensive investigations of these clusters have not been done yet.

The presence of  $C_{36}$  has also been predicted as one of the smaller fullerenes.  $C_{36}$  and the other carbon clusters,  $C_{2n}$  ( $2 \le 2n \le 100$ ), have been observed experimentally in jet-cooled cluster beam experiments by Cox and co-workers<sup>7</sup> and Smalley and co-workers.<sup>8</sup> The structures of  $C_{36}$  and other carbon clusters have been investigated by gas-phase mobility measurements by ion chromatography,<sup>9,10</sup> but the detailed structure and properties of  $C_{36}$  have not yet been clarified.

It was not until quite recently that the first fullerene smaller than  $C_{60}$ ,  $C_{36}$ , has been produced by the electric DC arcdischarge method by Zettl and co-workers.<sup>11</sup> They reported that a solid  $C_{36}$  was produced in a macroscopic quantity by the DC arc-discharge method with a graphite electrode in a 400 Torr helium atmosphere. They reported that the produced soot contained  $C_{36}$ . Their study suggested the presence of a fullerenelike caged  $C_{36}$  which exists as a covalently bonded clusterassembled material in the solid state. Theoretical calculations<sup>12–15</sup> also suggested that  $C_{36}$  form stronger inter-cage bonds than the normal fullerenes and the presence of various types of  $C_{36}$ -based oligomers in the solid state. The stability of  $C_{36}^{-}$  and  $C_{36}^{-2}$ was also studied theoretically.<sup>16</sup> Furthermore, Cohen and coworkers have calculated the electron—phonon interaction potential of a solid C<sub>36</sub> and predicted the possibility of a superconducting transition temperature larger than those of alkalidoped C<sub>60</sub> solids.<sup>17,18</sup> Various experimental attempts to reproduce the production of C<sub>36</sub> by the DC arc-discharge method, however, has not so far been successful, probably because the optimum arc-discharge and sublimation conditions on the production and purification of C<sub>36</sub> are still not known.

Recently, we have reported a high-yield and preparative-scale synthesis of  $C_{36}$  with purification and identification of  $C_{36}$  hydrides and the oxyhydrides ( $C_{36}H_6$  and  $C_{36}H_6O$ ) based on the high-temperature laser-vaporization (laser-furnace) method.<sup>19</sup> In this study, a distinct signal corresponding to  $C_{36}H_4$  was observed by laser desorption/ionization time-of-flight mass spectrometry (LD TOF-MS) in the soot produced by the laser-furnace method. We have found that the metal catalysts such as Ni/Co and Ni/Y significantly enhance the production of  $C_{36}$  species. It is well-known that these metals can enhance the production of single-wall carbon nanotubes (SWNTs).<sup>20</sup> It was also reported that purified  $C_{36}$  materials exist as a cluster-assembled material in the solid state, not as a molecular form such as  $C_{60}$ .

Here, we report the first successful production and characterization of C<sub>36</sub>-related materials (C<sub>36</sub>H<sub>4</sub>, C<sub>36</sub>H<sub>4</sub>O, C<sub>36</sub>H<sub>6</sub>, and C<sub>36</sub>H<sub>6</sub>O) by a new system (the laser-furnace LD TOF mass spectrometer) developed in this laboratory. We also report a large-scale synthesis of C<sub>36</sub>H<sub>6</sub> via the DC arc-discharge method with metal-doped graphite anodes. A matrix-assisted laser desorption/ionization (MALDI) TOF mass spectrometry with cobalt ultrafine particles (Co-UFP) has revealed that C<sub>36</sub>H<sub>6</sub> tends to dissociate into C<sub>18</sub>H<sub>3</sub> as a magic fragmentation on desorption/ ionization.

### **Experimental Section**

**High-Temperature Laser Vaporization (Laser-Furnace) TOF Mass Spectrometer.** The high-temperature laser vaporization (laser-furnace) method was originally developed by Smalley and co-workers for production of fullerenes and metallofullerenes.<sup>21</sup> The laser-furnace method is also a useful method

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**Figure 1.** A schematic diagram of the high-temperature laser vaporization LD TOF mass spectrometer.

for SWNT production when one employs a Ni/Co/graphite composite rod as a target rod.<sup>20</sup> However, details of the laser-furnace products besides SWNTs have not been thoroughly investigated to date.

Investigations of SWNT intermediates and its precursors are particularly interesting in understanding the growing mechanism of SWNTs. We have developed a new apparatus to produce and analyze soot containing C<sub>36</sub> materials,<sup>19</sup> which consists of a laser-furnace combined anaerobically with a LD TOF mass spectrometer. Figure 1 shows a schematic of the apparatus: the high-temperature laser vaporization LD TOF mass spectrometer. It consists of an electric furnace with a target rod in a quartz tube (28 mm inner diameter), a transferring chamber of a sample plate (15 × 15 mm) on which soot deposits, and a linear reflectron TOF mass spectrometer. Ni(0.6 at. %)/Co(0.6 at. %)or Ni(4.2 at. %)/Y(1.0 at. %)-doped graphite composite rods (Toyo Tanso Co. Ltd., 5 × 5 × 20 mm) were used for target rods.

The second-harmonic output of a Nd:YAG laser (532 nm, 10 Hz, 6–7 ns, 600 mJ/pulse, ca. 1 mm diameter spot; Spectra-Physics GCR-250) was used to vaporize the metal-doped graphite composite rod at a temperature range of 30-1000 °C in an Ar flow (1–760 Torr, 300 mL/min) condition. Special precaution was taken to vaporize the fresh surface of the target rod.

The soot containing C<sub>36</sub> species together with fullerenes and SWNTs were collected on a water-cooled nickel plate. The plate was anaerobically transferred to the acceleration region of the LD TOF mass spectrometer, which enable us to perform in situ TOF mass analyses. The mass analysis was done in the LD TOF MS chamber ( $\sim 10^{-7}$  Torr). The linear reflectron-type LD TOF mass spectrometer employs vertical laser desorption. The third-harmonic output of the other Nd:YAG laser (355 nm, 2 Hz, HOYA Continuum MINILIGHT II) desorbs and ionizes the soot product on the plate. The pulse sequence, such as the delayed time and the acceleration time of ions, was controlled by a pulse generator (SRS Inc. DG535). The acceleration voltage was typically set at 2400 V. The time-of-flight signals were analyzed by a transient digitizer (LeCroy 9400 A). The conversion from time-to-mass scale and the analysis of the obtained TOF spectra were performed on a personal computer (NEC PC9801-VX).

A Large-Scale Synthesis of  $C_{36}$  Species by the DC Arc-Discharge Method. The details of the arc-discharge apparatus



**Figure 2.** In situ mass spectra of the laser-furnace products. The production conditions are (a) pure graphite target rod, 500 Torr Ar; (b) Ni/Co/C composite target rod, 100 Torr Ar; (c) Ni/Co/C composite target rod, 500 Torr Ar.

with an anaerobic sampling/collection mechanism are described elsewhere.<sup>22–25</sup> Similar Ni/Y- or Ni/Co-doped graphite rods as those used for the laser-furnace experiments were used as the anode. The gap of the anode  $(15 \times 15 \times 250 \text{ mm})$  and the cathode (a carbon block) was typically set to 1 mm. The arc was sparked at 300 A in a He atmosphere of 400 Torr. The soot containing C<sub>36</sub> species was extracted by solvents such as toluene and CS<sub>2</sub>. The extracts were analyzed by a homemade LD TOF mass spectrometer and a mass spectrometer (SHIMADZU KOMPACT MALDI IV) at 337.1 nm. The soot containing SWNTs was also characterized by a scanning electron microscope (SEM) (JEOL JSM 6340F).

The separation and isolation of  $C_{36}$  species from fullerenes was done by a high-performance liquid chromatography (HPLC) (UV detection at 280 nm: JASCO PU-987, UV-970) with a PBB column ( $\phi$  20 × 250 mm, nacalai tesque) with a 100% CS<sub>2</sub> eluent. The separation and purification were done at 10 mL/min and 5 mL/min flow rate, respectively.

## **Results and Discussion**

Observation of  $C_{36}$  Species Produced by the Laser-Furnace Method. Figure 2 shows in situ LD TOF positive mass spectra of soot products produced by the laser-furnace method. Figure 2a-c was obtained under the conditions of pure graphite, Ni/Co-doped graphite (Ar 100 Torr), and Ni/Co-doped graphite (Ar 500 Torr), respectively. The temperature of the furnace was set at 1000 °C. Only fullerene signals corresponding to C<sub>60</sub>,



**Figure 3.** Expanded mass spectra of the  $C_{36}$  species produced by the laser-furnace method. The insert shows a calculated theoretical mass distribution of  $C_{36}H_4$ .

C<sub>70</sub>, and some higher fullerenes were observed. Of particular importance is the observation that the weak peaks at 436 and 452 amu (Figure 2b) were enhanced dramatically by using a Ni(0.6 at. %)/Co(0.6 at. %)/C composite rod at Ar 500 Torr (Figure 2c). The signal intensity of C<sub>36</sub>H<sub>4</sub> (436 amu) was enhanced 12 times as large as that in Figure 2b.

The intact  $C_{36}$  ion (432 amu) was not observed, and only the hydrides and oxyhydrides were detected.  $C_{36}$  must be quite reactive so that, immediately after its formation,  $C_{36}$  incorporates four hydrogen atoms on the reactive sites even though only a trace amount of hydrogen sources is present in the entire laser-furnace LD TOF MS combined system.

Figure 3a shows a high-resolution mass spectrum of the  $C_{36}$  species. The observed ion intensity distribution is consistent with that of the corresponding calculated theoretical ( $^{12}C = 98.9\%$ ,  $^{13}C = 1.1\%$ ) distribution as shown in the inset. Interestingly,  $C_{36}H_4$  and  $C_{36}H_4O$  in the as-produced soot were converted entirely to  $C_{36}H_6$  and  $C_{36}H_6O$ , respectively, upon CS<sub>2</sub> solvent extraction (Figure 3b). The peak intensity of the oxide species,  $C_{36}H_6O$ , has decreased after the extraction, probably because that the solubility of the oxide species in CS<sub>2</sub> is much less than that of  $C_{36}H_6$  species.

The observed transformation from the four-hydrogenated species,  $C_{36}H_4$ , to the six-hydrogenated species,  $C_{36}H_6$ , on the extraction suggests that two reactive sites were newly formed on  $C_{36}H_4$ , favorable to incorporate two additional hydrogen atoms. This may be due to bond-breaking of the solid composed of  $C_{36}H_4$  upon  $CS_2$  extraction, which may lead to the formation of a molecular  $C_{36}H_6$  species in solution.



Figure 4. A mass spectrum of the  $CS_2$  extract of the arc-discharge products with a Ni/Y/C composite electrode.

A similar enhancement of  $C_{36}H_6$  and  $C_{36}H_6O$  has been observed for Ni(4.2 at. %)/Y(1.0 at. %)-doped graphite rods but was not observed for Fe- and Ti-doped graphite rods. Namely, the formation of  $C_{36}$  species is efficiently catalyzed by exactly the same metal catalysts as in those for SWNTs. Furthermore, other laser-furnace conditions, such as laser fluence, Ar pressure, and furnace temperature, for the optimum production of  $C_{36}$  species are the same as those of SWNTs. This may lead us to speculate that the early stage of the formation of  $C_{36}$  species and that of SWNTs are closely related with each other.

A Large-Scale Production of  $C_{36}$  Species by DC Arc-Discharge. In this study, we have also found that the  $C_{36}$ species can be produced by the arc-discharge method of a metaldoped graphite electrode similar to the laser-furnace method. Figure 4 shows a positive LD TOF mass spectrum of a  $CS_2$ extract of a soot produced by arc-discharge of Ni/Y/C composite electrode under a He atmosphere of 400 Torr. Signals corresponding to fullerenes such as  $C_{60}$ ,  $C_{70}$ , and  $C_{84}$  were detected. The presence of an enhanced peak due to  $C_{36}H_6$  is particularly noticeable. In contrast to the laser-furnace case, the signal of oxide species,  $C_{36}H_6O$ , was not observed in the arc-discharge products.

Similar to the laser-furnace case, the optimum production of  $C_{36}$  species by the DC arc-discharge was achieved when the optimum production of SWNTs[Ni(4.2 at. %)/Y(1.0 at. %)]<sup>26</sup> was obtained. In general, a soot containing SWNTs shows a sheetlike or a weblike deposit. We found that the  $C_{36}$  species coexist with SWNTs in a weblike soot (deposit). Figure 5 shows a SEM image of the soot that contains the  $C_{36}$  species as observed in Figure 4. The SEM image shows bundles of SWNTs with diameters of ca. 10–100 nm. The formation of the thicker bundles is due to an enhanced bundle formation after extraction and purification.

Figure 6 shows an HPLC chromatogram of the CS<sub>2</sub> extract which corresponds to Figure 4. The peak due to  $C_{36}$  species (shaded area called as fraction 1) appears at ca. 6 min earlier than  $C_{60}$  and  $C_{70}$ . The  $C_{36}$  fraction was separated from  $C_{60}$ ,  $C_{70}$ , and the other higher fullerenes. Fraction 1 shows three sub-fractions, 1-1, 1-2, and 1-3, in the second HPLC stage on a PBB column as given in Figure 7.

Figure 8a–c shows MALDI TOF mass spectra of the fractions 1-1, 1-2, and 1-3, respectively, with a cobalt ultrafine particle (Co-UFP)<sup>27</sup> as a matrix. The C<sub>36</sub> species was contained in fraction 1-2. Fractions 1-1 and 1-3 mainly contain species having 524 and 219 amu, respectively. At present, we think the species due to 219 and 524 amu are reaction dissociation products of C<sub>36</sub> species.



Figure 5. A SEM image of the purified soot produced by DC arc-discharge of a Ni/Y/C composite electrode. Bundles of SWNTs are also clearly observed.



**Figure 6.** An HPLC chromatogram (10 mL/min flow rate) of the  $CS_2$  extract of the arc-discharge products with a Ni/Y/C composite electrode. The shaded area shows the HPLC fraction containing  $C_{36}$  species.



**Figure 7.** An expanded HPLC chromatogram (5 mL/min flow rate) of the  $C_{36}$  species fraction (the shaded area in Figure 6).

A Magic Fragmentation of  $C_{36}H_6$ . During the mass spectral analysis, we have found that  $C_{36}$  species have a strong tendency to fragment. In fact,  $C_{36}H_6$  was not observed by direct LD TOF mass spectrometry without matrixes. Figure 9(a) shows a LD



Figure 8. Mass spectra of HPLC fractions: (a), (b) and (c) show fraction 1-1, 1-2, and 1-3 in Figure 7, respectively.

TOF mass spectrum of the  $C_{36}$  species fraction (the shaded area in Figure 6) without matrixes. Only a signal due to 219 amu was observed, indicating that  $C_{36}H_6$  dissociates almost completely to give the 219 amu species. The 219 amu species can be assigned as  $C_{18}H_3$ , a half of  $C_{36}H_6$ . Obviously,  $C_{36}H_6$  is fragile upon desorption/ionization. In contrast, MALDI mass analysis of the same HPLC fraction by using Co-UFP and  $C_{60}$ as matrixes gave distinct peaks due to the parent  $C_{36}H_6$  ions, which is shown in Figure 9b,c, respectively. Evidently, the Co-UFP and  $C_{60}$  matrixes play crucial roles in dissipating excess



**Figure 9.** Mass spectra of (a) purified  $C_{36}H_6$ , (b) purified  $C_{36}H_6$  with Co ultrafine particles (Co–UFP) matrix, and (c)  $C_{36}H_6$  with  $C_{60}$  matrix.



Figure 10. A mass spectrum of a dried  $C_{36}H_6$  solid prepared by evaporating a purified  $CS_2$  extract.

energies upon desorption/ionization.  $C_{60}$  has been also known as an effective matrix for LD TOF MS.<sup>28</sup> The  $C_{60}$  molecules, which have a strong absorption at 328 nm close to the N<sub>2</sub> laser wavelength at 337 nm, effectively absorb the laser photons and effectively transfer the corresponding photon energy to  $C_{36}H_6$ 

A MALDI TOF mass spectrum of the purified solid-state  $C_{36}H_6$  with a higher laser fluence shows a series of peaks due to the oligomers of  $C_{36}$  (i.e.,  $C_{144}-C_{216}$ ) species and/or their fragments in addition to  $C_{36}H_6$  (Figure 10). It is highly likely that the purified  $C_{36}H_6$  forms oligomers or clusters immediately after the removal of solvent  $CS_2$  molecules owing to its very

high reactivity. Recent theoretical calculations<sup>13,14</sup> also suggest such an oligomer formation of  $C_{36}$ . The purified  $C_{36}$  species, on the other hand, can exist as a molecular form in Co-UFP or  $C_{60}$  matrix and does not bind together. Zettl and co-workers reported<sup>29</sup> that the pure  $C_{36}$  solid gave a very broad mass distribution peaked at about  $C_{120}$  and that the K-doped  $C_{36}$  solid showed a very sharp peak of  $C_{36}$  similar to the current MALDI TOF mass spectrum with the Co-UFP. Of particular interest in the present study is that  $C_{60}$  molecules prevent  $C_{36}$  species from aggregation and that they disperse molecularly the  $C_{36}$  species in the solid state or a concentrated solution.

#### Conclusions

We have found that  $C_{36}$  species were effectively produced not only by the laser-furnace method but the DC arc-discharge method with a metal-doped graphite composite rod containing Ni/Co and Ni/Y, respectively. In particular,  $C_{36}H_6$  was produced by arc-discharge in a large scale. The production conditions for the current  $C_{36}$  species are found to be similar to those of SWNTs in terms of metal catalysts, temperature, and Ar (or He) buffer gas pressure. A MALDI mass analysis reveals that a molecular  $C_{36}H_6$  gives  $C_{18}H_3$  as a magic fragment upon desorption/ionization.

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