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A STUDY OF PRECURSOR CLUSTERS OF SINGLE-WALLED CARBON NANOTUBES (SWNTS) BY FT-ICR MASS SPECTROMETER

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) [1] is now recognized as the most fascinating material of so-called nano-technology in this century. Despite the expectation of future applications, it is still difficult to obtain large amount of pure SWNTs, because the generation process is still not clear. It is well known that transition metals such as La, Y and Sc can be encapsulated inside the fullerene cage. On the other hand, transition metals such as Ni, Co or Fe are required to generate SWNTs. And the diameter distribution of SWNTs depends on the catalyst metal. However, the role of metal atom in the growth process of SWNTs is not yet known. In this paper, by using FT-ICR (Fourier transform ion cyclotron resonance) mass spectrometer [2], we studied laser-vaporized clusters from Ni/Co, Ni/Y and Rh/Pd (these metals were typical catalyst metals for SWNTs) loaded graphite samples.

The FT-ICR mass spectrometer used in this study was based on the design in Smalley's group at Rice University [2]. Metal/carbon binary clusters were produced by laser vaporization in cluster beam source. The cluster beam was directly injected to the magnetic field through a skimmer with the opening diameter of 2 mm and a deceleration tube. After deceleration, cluster ions were trapped by electric field in the ICR cell. And cluster ions were excited for the detection of the mass distribution.

Depending on metal species, generated cluster distributions were drastically different. In case of a Ni/Co doped carbon material, the peak of mass distribution appeared at relatively high mass range such as equivalent to C_{150}. On the other hand, for a Rh/Pd doped carbon material, the observed mass distribution of clusters were limited only up to C_{70}. This result can be clearly compared with the facts that SWNTs from Ni/Co doped sample has larger diameter such as 1.2 nm, in contrast to about 0.8 nm from Rh/Pd doped sample. Diameters of cage structured C_{150} and C_{70} are roughly 1.1 nm and 0.8 nm, respectively. Hence, it is speculated that the size of precursor clusters may determine the diameter of SWNTs. We propose that metal atoms affect the growth of clusters, and as a result, the final SWNTs diameter distribution is determined by the size of these precursor clusters.

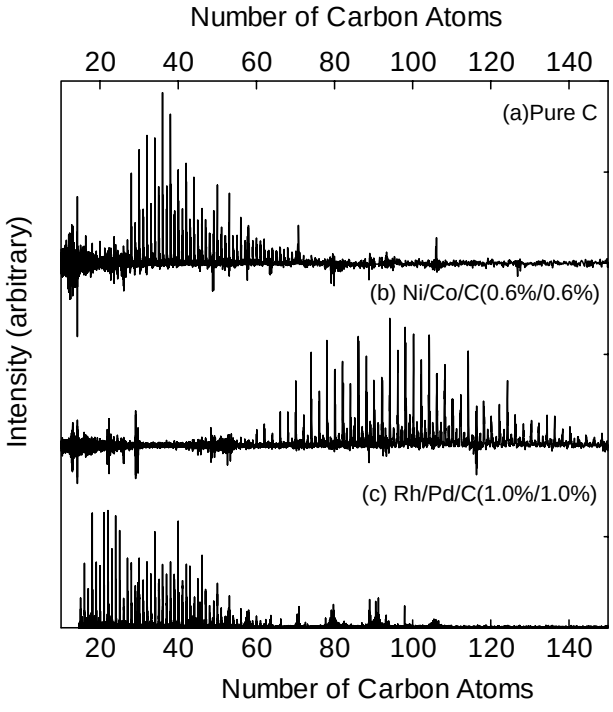

Figure A-1 FT-ICR mass spectra of as injected negative clusters from pure graphite and metal-doped graphite samples.

NOMENCLATURE

B:	Magnetic field
f:	Ion cyclotron resonance frequency
M:	Cluster ion mass
m:	Number of carbon atoms of a cluster
n:	Number of carbon atoms of a cluster
q:	Charge of cluster ion

INTRODUCTION

In 1985, when the existence of fullerene C_{60} and C_{70} were reported by Kroto et al. [3], this discovery of third allotropes of carbon excited a whole researchers. Later derivatives of fullerene such as hetero-fullerene [4], endohedral-metallo fullerene [5], and higher fullerene [6] are discovered and extensively studied. Various applications for fullerene are being explored such as a contrast medium of MRI [7,8], high temperature superconductor [9] or carriers of the medicine [10].

Afterwards, single-walled carbon nanotubes (SWNTs) was discovered by Iijima et al. [1] and the research became more and more popular as an essential new material. Carbon nanotube is classified into two types, one is SWNTs [1] and the other is multi-walled carbon nanotubes (MWNTs) [11]. The diameter is about 0.7 nm – 2.0 nm for SWNTs and 4 nm – 100 nm for MWNTs, and the length reaches an order of a few tens of μm. SWNTs are expected as a new material from various physical and chemical properties based on its geometric structure. As possible applications, electric wire for integrated circuits, field effect transistor, a field emission electron source for flat displays, a probe of AFM, a heat conduction element, conductive composite material and hydrogen storage material are discussed.

Despite many ideas of promising applications of SWNTs, the controlled synthesis and the bulk production at a low cost are still difficult. Even though many generation mechanisms of SWNTs (such as Kataura et al. [12] and Yudasaka et al. [13, 14]) are proposed, each idea is lacking for the decisive evidence. Especially, the role of catalytic metals such as Ni, Ni/Co, and Rh/Pd for laser-oven technique and Ni/Y for arc-discharge technique is still unknown.

By using a FT-ICR (Fourier transform ion cyclotron resonance) mass spectrometer directly connected with a laser vaporization cluster beam source, we have studied metal/carbon mixed samples, La/C, Y/C, Gd/C, Ce/C, Ca/C, and Sc/C [15, 16] for the generation machanism of endohedral metallofullerene. The metal-composite clusters showed magic numbers of MC_{44}, MC_{50}, MC_{60}, (M = La, Y, Sc, Gd, Ce). The even-numbered carbon atoms for metallofullerene and the minimum size of

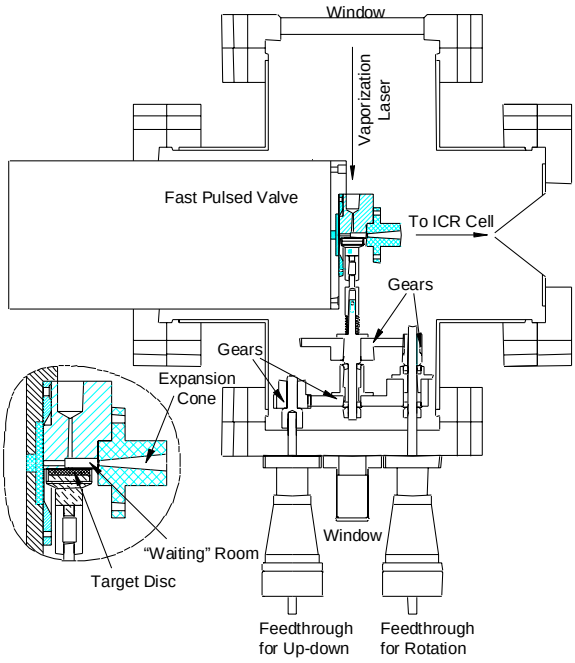

Figure 1 Laser-vaporization cluster beam source.

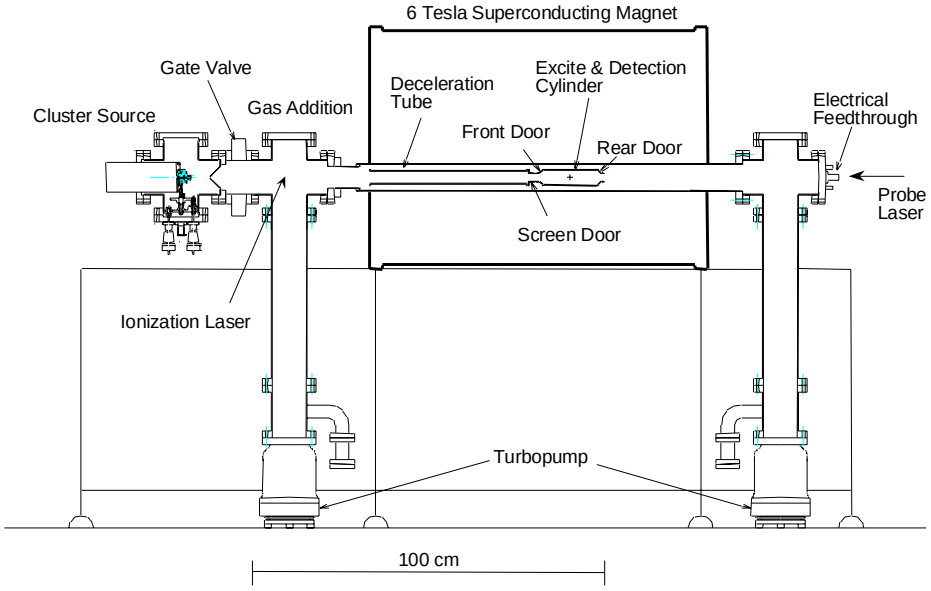

Figure 2 FT-ICR apparatus with direct injection cluster beam source.

di-metallic fullerene strongly suggested that all of these clusters had the caged form with one or two metal atoms inside.

In this report, we have studied metal-carbon binary clusters generated from Ni doped, Ni/Co doped, Ni/Y doped, and Rh/Pd doped graphite, which are used for the macroscopic generations of SWNTs by laser-oven or arc-discharge techniques.

EXPERIMENTAL

The experimental apparatus is based on the same design concept as the apparatus in Smalley's group [2] and the detailed characteristics are described in elsewhere [15-20]. Figure 1 and Fig. 2 show the cluster beam source and direct injection FT-ICR apparatus, respectively. The carbon cluster ion beam was generated outside of magnetic field by the laser-vaporization cluster beam source shown in Fig. 1. A pulsed gas valve, the sample motion mechanism and a skimmer were installed in a 6-inch 6-way UHV cross. A solid sample disk was vaporized by the focused beam of Nd: YAG laser (2nd harmonics) while timed pulsed gas was injected to the nozzle. In the atmosphere of helium gas, vaporized atoms condensed to clusters, and then, were carried and cooled by the supersonic expansion of helium gas. The cluster beam was directly injected to the magnetic field through a skimmer with the opening diameter of 2 mm and a deceleration tube [15].

The FT-ICR is the unique mass spectroscopy based on the ion-cyclotron motion of clusters in a strong magnetic field. The ion cyclotron frequency f is inversely proportional to the ion mass M as follows.

$$f = \frac{qB}{2\pi M} \tag{1}$$

Extremely high mass-resolution at high mass-range such as resolution of 1 amu at 10,000 amu range can be obtained. Furthermore, since the ions can be trapped in the vacuum for a few minutes, it is possible to perform the chemical reaction experiments. The ICR cell, 42 mm I.D. 150 mm long cylinder was placed in a stainless tube (SUS316) of 84 mm I.D. which penetrated the homogeneous 5.826 Tesla super-conducting magnet commercially available for NMR. Two turbo-pumps ($300\,\ell/s$) fore-pumped by a smaller turbo-pump of 50 ℓ/s were placed at the floor in order to avoid the effect

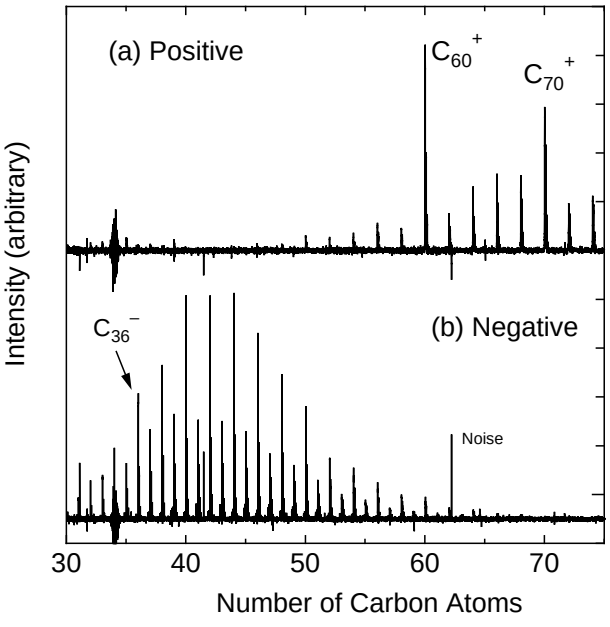

Figure 3 Positive (a) and negative (b) clusters generated from Ni/Co doped carbon materials.

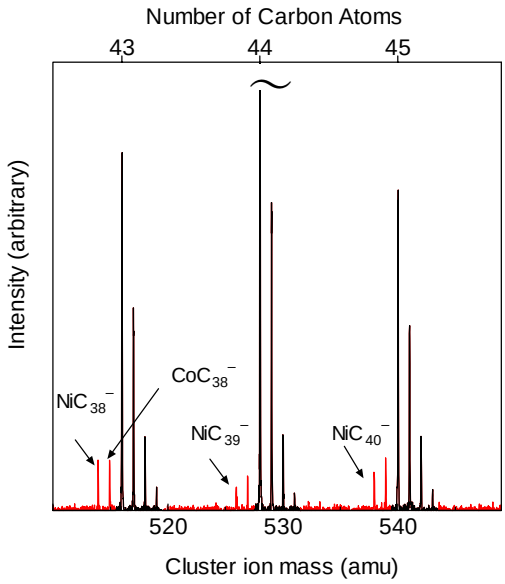

Figure 4 Expanded view of Figure3 (b).

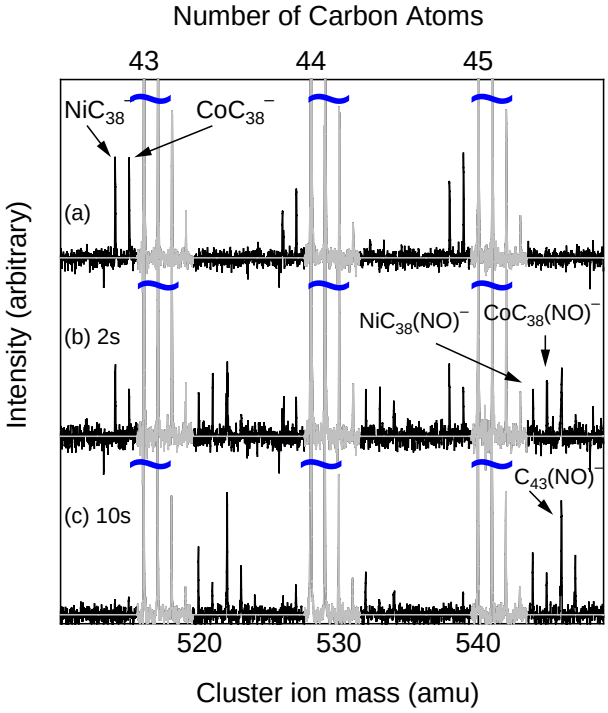

Figure 5 NO Reaction of NiC_{38}^- and CoC_{38}^- from Ni/Co doped sample.

of strong magnetic field. The typical background pressure was 3×10^{-10} Torr.

For the chemical reaction experiments, the kinetic energy of clusters was thermalized with room temperature argon gas at 10^{-5} Torr. Then, nitric oxide (NO) gas was supplied to the cell by a pulsed valve for a fixed period. The pulse value was adjusted so that the pressure at the ICR cell chamber became at 10^{-5} Torr for unreactive clusters and 10^{-7} Torr for reactive clusters. After pumping out, cluster ions were excited to detect the mass distribution.

RESULTS AND DISCUSSIONS

Figure 3 shows mass spectra of clusters generated from Ni/Co (0.6 at. % Ni and 0.6 at. % Co) doped carbon material used for the laser-oven SWNTs generation [21]. Positive (a) and negative (b) mass spectra as injected from the cluster beam source are shown in Fig. 3. There was not a trace of Ni or Co in the positive mass spectrum and C_{60}^+ and C_{70}^+ were observed as the magic number. This tendency was similar to the case of using pure graphite materials, though signals of C_{60}^+ and C_{70}^+ were much enhanced with this doped case. On the other hand, in the case of negative ions, tiny signals of NiC_n^- and CoC_n^- were measured in Fig. 4 (expanded view of Fig. 3(b)). Other drastic effect of doping of Ni/Co was observed in pure carbon cluster distribution. The even-odd alternations were observed from C_{36}^-. When the clusters were generated from the pure graphite materials, this even-odd alternation was not observed. There were some even-odd differences in the signal intensity of NiC_n^- and CoC_n^-; these peaks were stronger for even-numbered carbon clusters. However, this even-odd difference seems to simply reflect the relative abundance of pure carbon clusters.

The chemical reaction of these clusters with NO was used as the probe of the structure of clusters. Reaction with 10^{-7} Torr of NO gas for 2 s and 10 s for the case of Ni/Co doped sample are shown in Fig. 5. The chemisorption of NO to NiC_n^- and CoC_n^- were observed much faster rate than pure carbon clusters. After the reaction for 2 s, the product of C_nNO^- gradually appeared. Since it is expected to be more reactive if a metal atom is exposed to NO, the high reactivity of NiC_n^- and CoC_n^- strongly suggests that Ni or Co atom is outside the carbon cage.

The Ni/Y (4.2 % Ni and 1.0 % Y) doped carbon material optimized for the arc-discharge SWNT generation [22] was also studied. The positive mass spectrum shown in Fig. 6(a) was not distinguishable from the Y doped carbon material (0.8 % Y) used for the endohedral metallofullerene generation [16]. Most of clusters had one Y atom and even number carbon atoms, and YC_{44}^+, YC_{50}^+, YC_{60}^+ were observed as magic numbers. On the other hand, only small signals of pure carbon clusters such as C_{60}^+ and C_{70}^+ were observed. In the negative spectrum, however, small pure carbon clusters and Ni attached clusters in addition to YC_{2n}^- were observed. As shown in Fig. 7(a), abundance of Ni attached clusters were sometimes almost the half of odd-numbered pure clusters for around NiC_{40}, but Ni-attachment was not observed for large clusters more than 50 carbon atoms.

Figure 7 shows the reaction of binary clusters from Ni/Y doped sample with 10^{-5} Torr in NO gas for 5 s. It should be noted that the pressure of NO gas was 100 times higher compared with the case of Ni/Co doped samples. Even though tiny NiC_n^- clusters such as NiC_{44}^- or NiC_{46}^- were completely reacted away, the reaction of YC_{2n}^- such as YC_{42}^- with NO was not observed. Comparing signal heights of YC_{2n} and C_{2n}, it can be concluded that YC_{2n} is less reactive than pure carbon

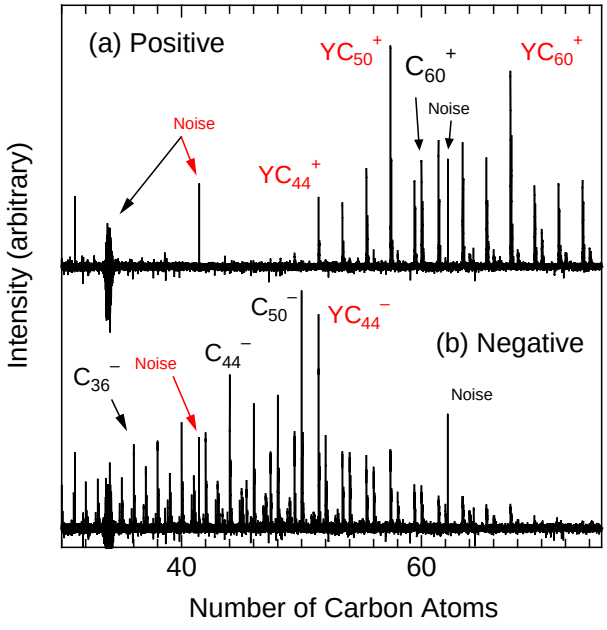

Figure 6 As injected positive (a) and negative (b) clusters from Ni/Y doped carbon material.

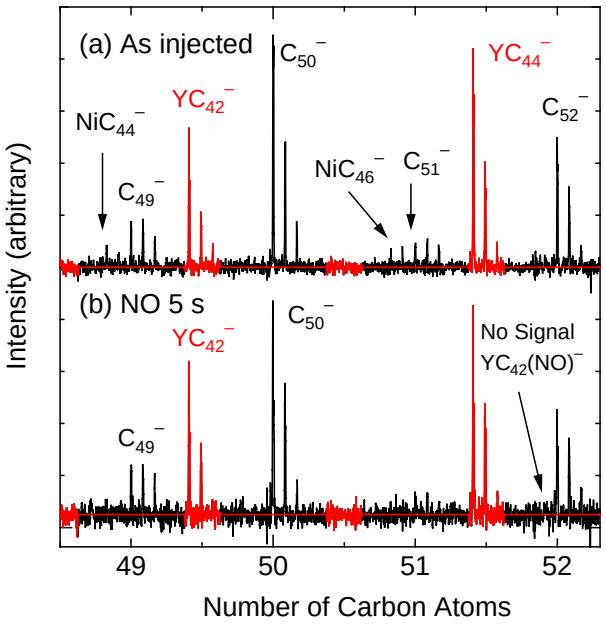

Figure 7 NO reaction of NiC_n^- and YC_n^- clusters from Ni/Y doped sample.

clusters. Hence, it is reasonable to assume that Y atom is inside the cage carbon cluster, just like the precursor clusters of endohedral metallofullerene [16].

Besides the experimental study, molecular dynamics simulations of growth process of binary clusters from randomly distributed carbon and metal atoms were performed [23]. The Y containing carbon cage cluster for Y-C system and carbon cage structure with Ni atom staying on a face for Ni-C system were predicted. These simulation results are completely consistent with experimental results.

Figure 8 is an example of detected positively charged cluster ions. Laser vaporized clusters from graphite materials, (a) pure graphite, (b) Ni/Co (0.6 at. % each) doped graphite, (c) Rh/Pd (1.0 at. % each) doped graphite, (d) Ni/Co (6.0 at. % each) doped graphite and (e) Ni (1.2 at. %) doped graphite were compared. Figure 8 shows metal-doped graphite samples are much easier to generate small clusters than pure carbon. Since metal-attached carbon clusters are observed in those small mass ranges, it is assumed that those metals have tendency to prohibit the further growth. This feature is completely opposite to the effect of metals used as endohedral metallofullerene such as La, Y, and Sc[16].

Figure 9 shows detected negatively charged cluster ions. Laser vaporized clusters from graphite material, (a) pure graphite, (b) Ni/Co (0.6 at. % each) doped graphite, (c) Rh/Pd (1.0 at. % each) doped graphite, (d) Ni/Co (6.0 at. % each) doped graphite and (e) Ni (1.2 at. %) doped graphite were compared. In case of Ni/Co (0.6 at. % each) doped carbon material, the peak of mass distribution appears at relatively high mass range such as equivalent to C_{150}, and Ni doped carbon material is also comparative. On the other hand, for Rh/Pd doped carbon material, observed mass distributions are limited only up to C_{70}. And the case of Ni/Co (6.0 at. % each) doped carbon material, observed mass distributions were further limited up to C_{50}. These results except for the case of Ni/Co (6.0 at. % each) are remarkably compared with the diameter distributions of macroscopic SWNTs generated with laser oven technique; peak diameter at 1.2 nm from Ni/Co doped graphite and at 0.8 nm from Rh/Pd doped graphite [12]. Diameters of cage structured C_{150} and C_{70} are roughly 1.1 nm and 0.8 nm, respectively. Hence, it is speculated that the size of precursor clusters may determine the diameter of SWNTs. Similar growth model has been proposed by Kataura et al. [12] that a collision of imperfect fullerene to a large metal-carbon binary particle leads to the nucleation of SWNT. Our molecular simulation [23] suggests that the imperfect fullerene clusters with a few metal atoms collide with each other to form some tubular structure.

From the cluster size distributions for Ni/Co (6.0%), the thin tube might be possible, if the quantity of Ni/Co doping is increased.

CONCLUSION

By using FT-ICR, mass spectrometric analysis and chemical reaction experiment of laser-vaporized metal carbon mixed sample have been performed. Depending

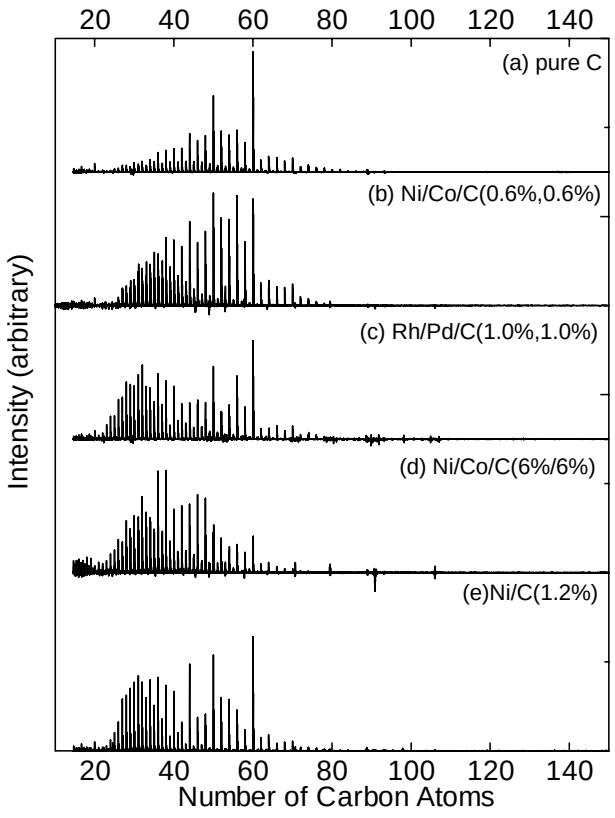

Figure 8 As injected positive carbon clusters.

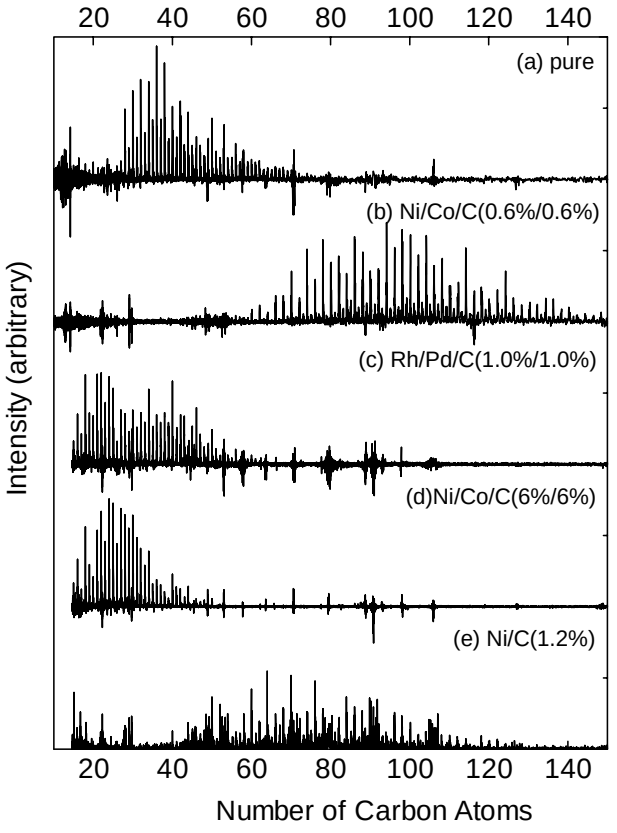

Figure 9 As injected negative carbon clusters.

on metal atoms, generated cluster distributions were drastically different. In case of a Ni/Co doped graphite material, the peak of mass distribution appeared at relatively high mass range such as equivalent to C_{150}. On the other hand, for a Rh/Pd doped carbon material, the observed mass distribution of clusters were limited only up to C_{70}. This result had a very good agreement with the fact that SWNTs from Ni/Co doped sample had larger diameter such as 1.2 nm, in contrast to about 0.8 nm from Rh/Pd doped sample. We considered that metal atoms affected the growth of the cluster, and as a result, the final SWNTs diameter distribution was determined by the size of these precursor clusters.

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